

UNPUBLISHED PRELIMINARY DATA

MORSE POTENTIAL FUNCTIONS FOR NONPOLAR GASES*

by

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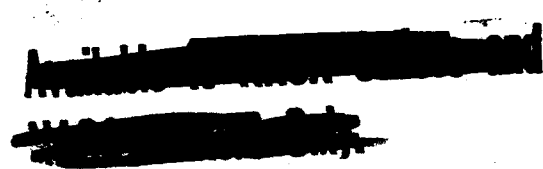
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Abstract

"Most likely" Morse potential functions for Ne, Ar, Kr, Xe, N₂, and CH₄ are determined from experimental second virial coefficient $[B(T)]$ and viscosity $[\eta(T)]$ data. By employing variants of the usual statistical fitting procedures, the elucidation of different features of the potentials is emphasized. Our "most likely" potentials give a better description of the experimental $B(T)$ and $\eta(T)$ and repulsive scattering potentials than do those based largely on crystal properties. The Morse potential is apparently less suitable than the Kihara potential for reproducing the experimental $B(T)$ and $\eta(T)$ at least for Ar; neither model is able to reproduce both properties within the limits of experimental error. A comparison is made with other selected model potentials.

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I. INTRODUCTION

Recently calculations have been made¹ of the second virial coefficient, $B(T)$, and its first two temperature derivatives in terms of the three-parameter Morse potential function:

$$\varphi(r) = \epsilon \left\{ \exp \left[-2(c/\sigma)(r - r_m) \right] - 2 \exp \left[(c/\sigma)(r - r_m) \right] \right\}.$$

Here, ϵ is the depth of the potential well at its minimum where $r = r_m$, the collision diameter σ defines the zero of the potential, $\varphi(\sigma) = 0$, and c is related to the curvature of φ at the minimum and is simply related to the length parameters through the expression

$$r_m = (\sigma/c) (c + \ln 2).$$

The significance of the parameters is discussed in more detail elsewhere.¹ Subsequently, Konowalow and Hirschfelder² (KH) attempted to establish the validity of the Morse function as an intermolecular potential function. They determined the potential parameters for some nonpolar molecules (Ne, Ar, Kr, Xe, N₂, CH₄) from crystal data and the single $B(T)$ datum nearest room temperature. They found that values of $B(T)$ calculated in terms of the Morse potentials so determined reproduced the experimental $B(T)$ for these

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1. D. D. Konowalow, M. H. Taylor, and J. O. Hirschfelder, Phys. Fluids 4, 622 (1961).
 2. D. D. Konowalow and J. O. Hirschfelder, Phys. Fluids 4, 629 (1961).

substances over a wide range of temperatures as well as did those calculated in terms of the Buckingham (exp-6) and Lennard-Jones (12-6) potentials. (The parameters for the latter two potentials were determined from experimental crystal, $B(T)$, and viscosity, $\eta(T)$, data.)³

In comparing these same three potentials, Saxena and Gambhir⁴ found that the overall agreement between the $B(T)$ both for pure gases and gaseous mixtures and calculations in terms of the Morse potential was superior to the agreement afforded by the other two potentials. At this point the Morse function, despite some reservations about the adequacy of its form for very small¹ and very large^{2,5} separations, held promise of correlating various physical properties better than the more commonly used models. Subsequently, it was found by Saxena and Bahethi⁶ that these same Morse potentials gave only indifferent agreement with the experimental transport properties; overall, they found little reason to prefer either the Morse or the (exp-6) model. This has led us to question whether the Morse potential is incapable of an adequate description of the transport properties, or whether the difficulty might lie elsewhere.

There is a growing body of evidence⁷ that the assumption of

3. E. A. Mason and W. E. Rice, J. Chem. Phys. 22, 843 (1954).

4. S. C. Saxena and R. S. Gambhir, Mol. Phys. 6, 577 (1963).

5. R. B. Bernstein, The Proceedings of the IIIrd International Conference on the Physics of Electronic and Atomic Collisions, London, (North-Holland Publishing Company, Amsterdam, 1964) p. 895.

6. S. C. Saxena and O. P. Bahethi, Mol. Phys. 7, 183 (1963).

7. L. Jansen and R. McGinnies, Phys. Rev. 101, 1301 (1956); 104, 961 (1956). L. Jansen, Phys. Rev. 125, 1798 (1962); Phil. Mag. 8, 1305 (1963).

additivity, central to the determinations from crystal data of the particular potentials we have discussed, may lead to serious errors. Thus, such potentials are all somewhat suspect. It may or may not be significant that Barker, Fock and Smith⁸ (BFS) found the difference between the experimental crystal lattice energy for Ar and their calculations (assuming additivity) in terms of the Kihara potential was not very different from Jansen's⁷ theoretical estimate of the effect of nonadditivity.

It is our object, therefore, to redetermine the Morse potentials only from selected properties of dilute gases and so to avoid the necessity of treating crystal properties. We discuss in Section II the construction of error discriminants designed to extract from experimental $B(T)$ and $\eta(T)$ data information regarding different regions of the potential function. In Section III we examine critically for each substance the multiplicity of potentials which may be inferred by emphasizing different aspects of the same collection of experimental data. For all but Ne, we expect that our treatment fixes a more or less "well-determined" set of potentials. Finally, in Section IV we choose a "most likely" set of Morse potentials and compare their gross features with a few other potentials.

II. DETERMINING THE POTENTIALS

A. Experimental Data Used

Prominent among the physical properties for gases commonly used to determine model intermolecular potential functions are: the

8. J. A. Barker, W. Fock, and F. Smith, Phys. Fluids 7, 897 (1964).

second and higher virial coefficients, and the transport coefficients. There is a firm theoretical basis for connecting the intermolecular potential function with these bulk properties of gases.⁹

For the molecules we wish to consider, only $B(T)$, of the virial coefficients, is known with sufficient accuracy over appreciable temperature ranges for our purposes. LeFevre¹⁰ has shown that $B(T)$ is of itself insufficient to specify a nonmonotonic potential. Keller and Zumino¹¹ have shown that, for a nonmonotonic potential with a single minimum, the high-temperature $B(T)$ determines the repulsive portion of the potential while the low-temperature $B(T)$ determines the width of the potential well as a function of the depth. While the potential may not be determined uniquely from $B(T)$ alone, some of its features may be found from $B(T)$ data which spans a sufficiently wide range of temperatures.

Of the transport properties, $\eta(T)$ is probably the most accurately known over appreciable ranges of temperature. It is well established that $\eta(T)$ is most sensitive to the nature of the repulsive portion of the potential, and only weakly dependent on the attractive portion. It is for this reason that little significance can be attached to potentials determined solely from $\eta(T)$ data.

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9. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, The Molecular Theory of Gases and Liquids, Second Printing, (John Wiley and Sons, Inc., New York, 1964).

10. E. J. LeFevre, Department of Scientific and Industrial Research, Mechanical Engineering Research Laboratory, East Kilbride, Glasgow. Heat Division Paper No. 129 (1957).

11. J. B. Keller and B. Zumino, J. Chem. Phys. 30, 1351 (1959).

We assume, as did BFS in their determination of the Kihara potential parameters for Ar, that $B(T)$ and $\eta(T)$ data are sufficient to fix uniquely the intermolecular potential. This is probably a reasonable assumption to make in the case of Ar. We shall reexamine it in Section III for each of the substances we treat. The experimental data we have used together with their original sources are listed elsewhere.¹² Certain salient features of these data are listed in Table I. We note, for example, that for all the substances we consider except Ne there exist fairly reliable $B(T)$ data for temperatures spanning the Boyle temperature T_B . (Recall that $B(T_B) = 0$.) For Ne the few data that exist for $T < T_B$ appeared to be unreliable and was not used. For CH_4 , Kr, and Xe there is a paucity of high-temperature $\eta(T)$ data. For both Ar and N_2 both the $B(T)$ and $\eta(T)$ data extend over a wide range of temperatures.

Now let us consider the methods which may be used to extract from such data sufficient information to establish the approximate features of the intermolecular pair potential functions for a few nonpolar gases.

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12. Appendix I of this report.

TABLE I
SUMMARY OF EXPERIMENTAL DATA USED

Substance	Temperature Range ($^{\circ}\text{K}$)		T_B^a ($^{\circ}\text{K}$)	No. of Data Points	
	$B_x(T)$ data	$\eta_x(T)$ data		$B_x(T)$	$\eta_x(T)$
Ar	85-873	89-1978	410	35	40
N_2	90-673	111-1711	325	26	43
CH_4	108-673	122- 366	510	22	23
Kr	108-873	144- 366	560	23	11
Xe	273-973	278- 555	770	11	9
Ne	123-973	33-1066	<123	14	37

a Approximate Boyle Temperature

B. Error Discriminants

Among the most common methods for fixing the adjustable constants of a model potential function is to obtain a "best fit", in some sense, of one or more experimental properties by calculations made in terms of that potential. For a single, experimental, temperature-dependent property, $P_x(T)$, it is usual to adjust the potential parameters until some error discriminant, usually the standard deviation, $SD(P)$,

$$SD(P) = \left\{ \sum_i^{N(P)} [P_x(T_i) - P_c(T_i)]^2 / N(P) \right\}^{1/2} \quad (1)$$

is minimized. Here, $P_x(T_i)$ is the experimental value of the property P at the temperature T_i , $P_c(T_i)$ is the corresponding value calculated in terms of the model potential, and $N(P)$ is the number of such data points treated.

For calculated values, $B_c(T)$, of the second virial coefficient we used the algorithms developed previously^{1,13} for the Morse potential. We calculated $\eta_c(T)$ from the expression

$$\eta_c(T) \times 10^7 = \frac{266.93 (MT)^{1/2} f_{\eta}^{(3)}(c, T^*)}{\sigma^2 \Omega^{(2,2)*}(c, T^*)}$$

where M is the molecular weight, $T^* = kT/\epsilon$ where k is the Boltzmann constant, and $f_{\eta}^{(3)}(c, T^*)$ and $\Omega^{(2,2)*}(c, T^*)$ are functions of the Morse parameters c , and ϵ tabulated by Lovell

- 13. Erratum. In Table VI of Ref. 1 $a_{03}^{(2)} = -0.483986$ not -0.443986 . With this change the $F_0^{(2)}$ of Table IV, Ref. 1 can be correctly reproduced.

and Hirschfelder.¹⁴

An alternate approach is to obtain a "best fit" of $P_x(T)$ by minimizing the root-mean-square percentage error, $e_3(P)$, where

$$e_3(P) = 100 \left\{ \sum_i^{N(P)} \left[\frac{P_x(T_i) - P_c(T_i)}{P_x(T_c)} \right]^2 \right\}^{1/2} \quad (2)$$

(A useful refinement of either of these error measures is to weight the individual errors inversely as their relative precision. All too often, however, such a procedure is not feasible because the precisions are unknown.)

It is quite well known that potentials fixed by fitting a number of physical properties for a substance singly may be in serious disagreement with each other. It is necessary, therefore, to establish means whereby two or more properties may be considered in parallel in such a way that the potential may be relatively realistic.

The extension of the $e_3(P)$ criterion to the simultaneous

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14. S. E. Lovell and J. O. Hirschfelder, University of Wisconsin Theoretical Chemistry Laboratory Reports WIS-AF-19 and WIS-AF-21 (1962). Similar calculations have been reported by F. J. Smith and R. J. Munn, University of Maryland Institute of Molecular Physics Report IMP-NASA-39, August 12, 1964. The two sets of tabulations agree well except for $c = 8$ and $c = 10$ and for the very lowest reduced temperatures $T^* \approx 0.2$. Our calculations were essentially complete when this latter work became available; we have not repeated our calculations in terms of these most recent tabulations. Even if they turned out to be more nearly correct it would have little or no effect on the potentials we determine.

fitting of two or more temperature-dependent properties is straightforward; that for the standard deviation may be extended with some modification. Thus, it might be reasonable to fix the parameters of a model potential by minimizing the sum $\sum_P e_3(P)$. If for no other than aesthetic reasons, the $SD(P)$ needs to be cast in dimensionless form before being combined in a similar manner. Of the various ways this may be accomplished, we shall consider only two: the first is to define

$$e_1(P) = 100 \left[SD(P) \right] / \sum_i^{N(P)} \left[P_x(T_i) \right]^2 ; \quad (3)$$

the second is to define

$$e_2(P) = \left[N(P) \right]^{\frac{1}{2}} e_1(P) \quad (4)$$

which is only implicitly a function of $N(P)$. Thus, in the sense that any of

$$E_n \propto \sum_P e_n(P) , \quad n = 1, 2, \text{ or } 3, \quad (5)$$

is a minimum with respect to variation of all its parameters, a model potential function may be considered to give a "best fit" simultaneously to a number of different temperature-dependent properties.

We may argue that the E_n of Eq. (5) should be modified to take cognizance of the fact that the various $P(T)$ may be known

over widely different ranges of temperature. Thus each $e_n(P)$ should be weighted according to the extent, ΔT_p , of the temperature range for which $P_x(T)$ data is used. That is,

$$E_n = \sum_p \tau_p e_n(P) \quad , \quad (6)$$

where $\tau_p = (\Delta T_p) / \sum_p (\Delta T_p)$. This admittedly arbitrary weighting is based on the heuristic argument that a property is "better known", and thus has more to tell about the intermolecular potential, the wider the temperature range over which it has been measured. One weakness of this weighting is that the $e_n(P)$ corresponding to a property known at only a single temperature, is given zero weight. In a more realistic scheme such a datum would be taken properly into account. This is no serious fault in the present work since we consider only properties known over appreciable temperature ranges. Another desirable refinement to Eq. (6) would be to adjust the relative weighting of the $e_n(P)$ according to the relative overall accuracy with which the various properties are known. Such a refinement was not feasible because the accuracies of much of the data we used is unknown.

It is evident that the various $e_n(P)$ are closely related. For example, Eq. (3) may be rewritten in the form:

$$e_1(P) = 100 \left\{ \frac{1}{N(P)} \sum_{i=1}^{N(P)} \left[\frac{P_x(T_i) - P_c(T_i)}{P_x(T_i)} \right]^2 \omega_i \right\}^{\frac{1}{2}} \quad , \quad (3-a)$$

where

$$\omega_i = \left[P_x(T_i) \right]^2 / \sum_j \left[P_x(T_j) \right]^2 \quad (3-b)$$

Thus, $e_1(P)$ is no more than $e_3(P)$ modified to weight the fractional error at each temperature T_i proportional to the square of the magnitude of the datum $P_x(T_i)$. We call $e_1(P)$ and $e_2(P)$ weighted percentage errors. In contrast, for $e_3(P)$, the weighting of the individual percentage errors is unity.

A practical consequence of using either of the weighted percentage errors in an automatic computation is that properties (such as $B(T)$ or the Joule-Thompson coefficient) which pass through a zero may be treated without the danger of the error measure "blowing up"; $e_3(P)$ suffers an obvious defect in this respect. Of even greater consequence is the fact that, especially for a property whose magnitude varies appreciably as a function of temperature, the errors associated with the data of the largest magnitudes dominate the value of $e_1(P)$ or $e_2(P)$. Errors associated with data of small magnitude make relatively little contribution. With $e_3(P)$, data of varying magnitudes are ostensibly treated in a more egalitarian manner. Yet, as noted above, it may be inordinately sensitive to data in the neighborhood of a zero.

So far the discussion of the various error discriminants has been kept purposely general. Now let us examine the implications of using each of the E_n of Eq. (6) to "determine" the inter-

molecular potential function from only $B_x(T)$ and $\eta_x(T)$ data. With the single exception of Ne, for the substances we treat, both E_1 and E_2 depend most strongly on fitting the low-temperature $B_x(T)$ and the high-temperature $\eta_x(T)$ which are themselves most sensitive to the attractive and repulsive regions of the potential respectively. From this we may expect that potentials determined by minimizing either E_1 or E_2 may be relatively realistic over a wide range of separations. E_3 , on the other hand, depends most heavily on fitting the low-temperature $\eta_x(T)$ and the $B_x(T)$ in the region of T_B . Clearly, E_3 is most sensitive to a rather different region of the potential (that is, to separations $r \approx \sigma$ in the immediate vicinity of the zero of the potential) than is either E_1 or E_2 . We should be ill-advised to place too much confidence in the relevancy of potentials determined by minimizing E_3 alone since it apparently is sensitive to such a comparatively small range of the potential. Finally, in the event the potentials determined by all three E_n are sufficiently similar, we may more safely assume that the composite potential is a reasonable approximation to the true potential. How well these expectations are borne out is discussed in Section III.

C. Mathematical Technique (For Fixing the Morse Potential Parameters)

The error E , which here stands for any of the E_n defined by Eq. (6), is a function of the Morse parameters ϵ , c , and σ ; viz.,

$$E = E(\epsilon, c, \sigma) = E(\rho_1, \rho_2, \rho_3) . \quad (7)$$

We fix these parameters by requiring that E be a minimum with respect to their variation. Thus, we seek the solution to the system of equations

$$\partial E / \partial \rho_j = 0, \quad (8)$$

where ρ_j represents the various potential parameters. In general, Eqs. (8) are nonlinear, so a numerical solution is necessary. The method we used was an adaptation of the quadratic minimization procedure described by Ransil.¹⁵ We give only a brief outline of the method here.

Assuming the parameters ρ_j to be independent variables, E may be expanded about an arbitrary point near the minimum E_0 as follows:

$$E = E_0 + \sum_j (\partial E / \partial \rho_j)_0 \Delta \rho_j + \frac{1}{2} \sum_j \sum_k (\partial^2 E / \partial \rho_j \partial \rho_k)_0 \Delta \rho_j \Delta \rho_k + \dots (9)$$

By combining Eq. (8) and Eq. (9) we obtain the linear system of equations

$$(\partial E / \partial \rho_j) + \sum_k (\partial^2 E / \partial \rho_j \partial \rho_k) \Delta \rho_k = 0. \quad (10)$$

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15. B. J. Ransil, Rev. Mod. Phys. 32, 239 (1960).

Input to the minimization program are an initial guess of the parameter set ρ_j and the increments $\Delta\rho_k$ are needed to approximate the derivatives with the usual finite-difference forms. Eq. (10) is solved for the improved increments $\Delta\rho_k$, and the procedure is repeated until convergence is achieved.¹⁶

As is common to approximation methods such as this one, it is essential that the initial guess of the input parameters ρ_j lie reasonably close to those corresponding to the minimum for the procedure to converge. An underlying assumption of the quadratic minimization procedure is that a unique, well-defined minimum exists, or at least multiple minima are sufficiently well separated if they occur at all. We have further assumed that the minimum condition, Eq. (8), corresponds to a unique set of potential parameters. These points will be examined individually for each substance in the next section.

III. DISCUSSION OF RESULTS

In Table II are listed the Morse parameters which have been fixed by minimizing the various E_n of Eq. (6). (Neither for Kr nor for Xe were we able to fix a potential by minimizing E_3 with a reasonable expenditure of computer time because of the extreme sensitivity of the automatic minimization procedure to the relative error, $[B_x(T) - B_c(T)] / B_x(T)$, in the region of the Boyle point. These practical considerations serve to reinforce our previous contention of the unsuitability of E_3 . This variation is not entirely surprising in that the three E_n weight various temperature

16. The values of the Morse potential parameters listed in Table II were stable to at least the number of figures quoted there.

TABLE II

MORSE POTENTIAL FUNCTIONS FIXED BY VARIOUS CRITERIA

e/k (°K)	c	σ (Å)	n^b	Error ^a E_n^b	$SD(B)^a$ (cm ³ /mole)	$e_3(B)^a$	$SD(\eta)^a$ (10 ⁷ gm/cm sec)	$e_3(\eta)^a$
Ar								
132.64	5.064	3.5440	1	0.6193	3.7002	97.071	186.31	6.3357
143.80	5.363	3.4867	1	0.6266	4.7258	108.44	170.16	5.8544
134.65	5.118	3.5334	2	3.8465	3.8847	99.495	182.98	6.2576
132.59	5.064	3.5477	2	3.8482	3.7108	97.556	186.13	6.3522
128.11	4.673	3.4791	3	5.8862	4.4232	4.0555	413.00	6.6545
144.8	5.0	3.386	0	1.3603	7.1919	5.2868	426.74	6.6665
N ₂								
120.27	5.238	3.7153	1	0.6033	1.4162	78.04	142.83	6.3165
129.48	5.506	3.6654	1	0.6128	1.8937	92.67	135.11	6.1097
125.83	5.406	3.6879	2	3.7883	1.7677	91.61	136.38	6.2756
120.36	5.247	3.7184	2	3.7934	1.5089	83.54	141.02	6.4060
134.94	5.482	3.5891	3	4.9386	1.8766	3.029	200.40	5.6347
134.4	5.5	3.579	0	0.8388	1.4255	5.019	210.53	5.6565
CH ₄								
221.03	5.561	3.5097	1	0.3166	1.8662	42.05	10.755	1.5405
222.65	5.592	3.5036	2	1.4994	1.9225	40.13	9.938	1.3902
214.5 ^c	5.57	3.63	3	3.9279	4.0422	2.797	55.017	6.3094
177.5	4.9	3.683	0	1.2591	8.2883	29.949	26.911	3.9590
Kr								
199.18	4.898	3.5631	1	0.2440	1.7906	66.36	36.9452	2.1467
199.59	4.905	3.5609	1	0.2440	1.8003	65.98	36.6996	2.1149
199.33	4.901	3.5625	2	0.9993	1.7933	65.98	36.8761	2.1398
182.7	4.5	3.510	0	1.4516	14.4596	207.78	132.6792	5.2449

a. Values listed may be significant to only the first two or three figures.

b. $n = 1, 2, 3$ correspond to the n defined by Eqs. (2-4) and (6). $n=0$ corresponds to the procedure used by KH (Ref. 2); the value of E_1 is listed in the column labeled E_n .

c. Incompletely minimized.

TABLE II (continued)

ϵ/k (°K)	c	σ (Å)	n^b	Error ^a E_n^b	SD(B) ^a (cm ³ /mole)	$e_3(B)^a$	SD(η) ^a (10 ⁷ gm/cm sec)	$e_3(\eta)^a$
Xe	274.00	3.9477	1	0.4651	0.8824	82.61	57.666	2.3777
	272.26	3.9533	1	0.4652	0.8713	80.05	58.774	2.4234
	265.15	3.9787	2	1.4803	0.8080	57.51	65.422	2.6795
	274.7	3.872	0	0.9161	2.1246	544.51	75.318	2.0496
Ne	70.462	2.5982	1	0.3645	0.1922	3.6494	62.0966	2.5662
	74.779	2.5807	2	1.7085	0.2144	4.0387	54.7063	2.5162
	73.992	2.5781	3	2.8722	0.1911	3.3211	64.1362	2.5029
	43.99	2.775	0	1.2916	0.6971	19.4859	213.1332	4.5763

a. Values listed may be significant to only the first two or three figures.

b. $n = 1, 2, 3$ correspond to the n defined by Eqs. (2-4) and (6). $n=0$ corresponds to the procedure used by KH (Ref. 2); the value of E_1 is listed in the column labeled E_n .

ranges of $B(T)$ and $\eta(T)$ so differently. Somewhat more disturbing, however, are the several instances where two rather different sets of parameters give essentially identical values of either E_1 or E_2 . This apparent lack of uniqueness is most pronounced for Ar and N_2 . Indeed, the similarity between the two cases is so striking that a number of other observations may be made in common.

A. Ar and N_2

Firstly, the relative differences between the two lowest E_2 indices, about one part in one thousand, are hardly significant.¹⁷ Thus, the parameter sets are entirely equivalent under E_2 . Secondly, the relative differences in the two E_1 indices are about an order of magnitude larger and probably provide a clear choice for the set of parameters corresponding to the lowest E_1 . Now it is seen from Table II that there is for both Ar and N_2 an essential concordance between the parameter sets corresponding to the smallest E_1 and those corresponding to the (insignificantly) next smallest E_2 . In view of the rather different relative weighting given by E_1 and E_2 to the fit of the $B(T)$ and $\eta(T)$ data (especially in the case of N_2) the virtual coincidence of the parameter sets fixed under these two criteria is encouraging.

This rather sanguine view is subject to immediate reappraisal since the parameters determined by minimizing E_3 are appreciably different from those suggested by both E_1 and E_2 . Here, we were unable to find any but the single set of parameters, indicated

17. H. Margenau and G. M. Murphy, The Mathematics of Physics and Chemistry (D. Van Nostrand Company, Inc., New York, 1943).

in Table II, which minimized E_3 . The corresponding potential is in this sense unique. Let us recall that by its nature E_3 is inordinately sensitive to fitting the few $B(T)$ data in the neighborhood of T_B . Thus, in Table II we note that when E_3 instead of E_1 or E_2 is minimized there results a 25- to 30-fold decrease in the mean percentage error for $B(T)$ $[e_3(B)]$ and little sensible change in that for $\eta(T)$; concomitantly, there is about a 20 per cent increase in the standard deviation for $B(T)$ $[SD(B)]$ and roughly a doubling in that for $\eta(T)$. In Figs. 1-6 there is shown in detail the differences in the error curves $P_x(T) - P_c(T)$ vs. T when E_1 (or E_2) and E_3 are minimized. It is evident that the E_3 minimization forces good agreement between $B_x(T)$ and $B_c(T)$ in the region of T_B , and that there is worse agreement with both the low-temperature $B(T)$ and the high-temperature $\eta(T)$ than when E_1 or E_2 is minimized. In consequence, we should expect that the E_1 parameters allow a better description of $B(T)$ for $T < 90^\circ\text{K}$ and $\eta(T)$ for $T > 1700^\circ\text{K}$ than would the E_3 parameters.

The emphasis lent the high-temperature $\eta(T)$ and the low-temperature $B(T)$ in minimizing either E_1 or E_2 tends to make maximal use of the potential information content of these two properties. Thus, the Morse potentials so deduced are probably as close to "reality" as possible under the restrictions we have imposed. Of course, one test of the "reality" or "goodness" of a model potential function is its ability to describe adequately properties other than those from which it was determined. We shall

not consider this question in detail here. We note, however, that data in two temperature ranges are essentially ignored in both the E_1 and E_2 fitting procedures: $B_x(T)$ in the neighborhood of T_B and $\eta_x(T)$ for very low temperatures. We may use the agreement between experiment and calculations in these temperature ranges as a partial test of the goodness of the model. It is seen in Figs. 1-6 that such agreement is only fair at best for Ar and N_2 .

If, once again, we turn our attention to Table II we see that Ar and N_2 are different from the other substances we have considered in that the viscosity extends to quite high temperatures ($T^* \approx 15$) and that the agreement with experiment is well outside the bounds of experimental error which is estimated to be no more than 2 per cent. One possible explanation might be that the repulsive portion of the Morse potential is totally inadequate to explain such high temperature behavior. In a later section we shall examine the repulsive region of the potentials considered here.

B. Kr, Xe and CH_4

In the spirit of our earlier discussion of the information content of the $B_x(T)$ and $\eta_x(T)$ data we note sufficient similarity in the corresponding (reduced) temperature ranges for which these data are available that it is fruitful to discuss Kr, Xe, and CH_4 together. As we have already noted, there is a surprising paucity of high-temperature $\eta_x(T)$ data for all three substances. The $B_x(T)$ data on the other hand span the Boyle temperature and extend

to relatively low temperatures. For these substances, therefore, it is perhaps not quite so certain as it was in the case of Ar and N₂ that minimizing either E₁ or E₂ will tend to extract the maximal information content from the available B_x(T) and $\eta_x(T)$ data, and at the same time provide a severe test of the Morse potential.

It is seen in Table II that for all three substances the potentials fixed by minimizing E₁ and E₂ are fairly consistent. For Kr, the two potentials found by minimizing E₁ are very nearly identical, and are quite close to the potential fixed by minimizing E₂ despite the rather different weighting given the B(T) and $\eta(T)$ data in the two cases. Indeed, the parameters agree within a few tenths of a per cent. This is in marked contrast to the situation that was encountered with Ar and N₂.

For Xe, we found two fairly distinct potentials which admitted very nearly the same E₁. Here, the difference between E₁ and E₂ in weighting the B(T) and $\eta(T)$ data is much less pronounced than in the case of Kr, yet the Xe potentials fixed by these two criteria are considerably more different than they are for Kr. We interpret this behavior as an indication that the Xe potential is not so well determined as is the Kr potential. We expect that it would be necessary to know B_x(T) at temperatures down to ca. 170°K before we could fix the Xe potential even as well as we have the Kr potential.

The effective CH₄ potentials determined from E₁ and E₂ are not nearly as similar as one might expect from the fact that the data are weighted almost identically in the two cases. This

indicates that the CH_4 potential may be better determined than that for Xe but perhaps slightly less well determined than that for Kr.

For Kr, Xe and CH_4 we attempted to fix the potentials by minimizing E_3 as we had done for Ar and N_2 . We abandoned the attempt, however, since it was requiring too great an expenditure of computer effort. (Recall our previous comments of the sensitivity of E_3 to the $B_x(T)$ in the vicinity of T_B .) In Table II the potential for CH_4 corresponding to the minimization of E_3 is only approximate. It is sufficient to show, as we do in Figs. 7-9, that the main effect of minimizing E_3 instead of E_1 or E_2 is here no different than it was for Ar or N_2 ; namely, to force a good fit of $B_x(T)$ in the vicinity of T_B . Overall, however, the fit of both $B_x(T)$ and $\eta_x(T)$ is considerably worse with the E_3 potential than with either the E_1 or E_2 potential. We compare in Figs. 10 and 11 experimental and calculated values of $B(T)$ and $\eta(T)$ for Kr, and make the like comparison for Xe in Figs. 12 and 13.

C. Neon

The potential for Ne, alone of the substances we consider, is probably not well determined. Since the few $B_x(T)$ available for $T < T_B$ appear to be somewhat uncertain, we considered $B_x(T)$ only for $T > T_B$. Thus, in the spirit of our previous discussions, we can have only limited confidence in the Ne potentials determined here. This lugubrious view is taken despite the fact that the Ne

potentials listed in Table II determined by minimizing E_1 , E_2 , and E_3 agree fairly well among themselves and are compatible with the experimental data from which they were determined (see Figs. 14-16). Here, it appears that $B_x(T)$ data at temperatures down to ca. 40°K are necessary to determine a reasonably accurate potential for Ne by our methods.

IV. COMPARISON WITH OTHER POTENTIALS

Let us first compare the Morse potentials obtained here from gas properties with those² determined earlier largely from crystal properties. The latter are included in Table II as the last entry for each substance. It takes only a cursory glance to show that, on the whole, the "crystal-determined" potentials give a description of $B(T)$ and $\eta(T)$ inferior to that afforded by the potentials determined here. This result was anticipated on the basis of the arguments presented earlier and the comparisons made by Saxena and Bahethi.⁶ What was not expected, however, was the relatively small improvement in the agreement with viscosity data in a number of cases. This leads us to inquire whether the nature of the repulsive limb of the Morse potential precludes a realistic description of high energy behavior.

We know from the work of Buckingham,¹⁸ for example, that for very small separations the correct potential is of the form

$$\psi(r) \propto (1/r) \exp(-r) .$$

18. R. A. Buckingham, Trans. Faraday Soc. 54, 453 (1958).

At somewhat larger separations, however, high energy scattering experiments indicate that either an inverse power or else an exponential form may be suitable. Abrahamson's¹⁹ theoretical Thomas-Fermi-Dirac (TFD) potentials are also essentially exponential for a wide range of separations. Since the Morse potentials have an exponential repulsion, a comparison with these other potentials is of some interest. Unfortunately, for the interactions under consideration, there is only a very small overlap between the energies at which the scattering, TFD, and Morse potentials are valid. (For any of the latter the limit of validity is defined by $\varphi_{\max} = kT_{\max}$ where T_{\max} is the highest temperature for which data was used to fix the potential. See Table I.) Therefore, it may be necessary to extrapolate the Morse potentials to energies higher than those for which they are strictly valid in order to compare with the TFD and scattering potentials. The latter are examined in some detail elsewhere.^{19,20} In Figs. 17-22 we make the suggested comparisons on plots of $\log \varphi$ vs. r . The best one can hope to learn from these plots is whether the slope of a given Morse potential is approximately correct. Since $\partial \ln \varphi / \partial r \approx -2c/\sigma$, for r sufficiently small, the slope is sensitive to the parameter ratio c/σ . Unless the slope is very nearly correct, very little can be learned from such plots about the parameter ϵ which affects the vertical displacement of the Morse curves. Since we are comparing the Morse potentials with completely repulsive potentials,

19. A. A. Abrahamson, Phys. Rev. 130, 693 (1963).

20. I. Amdur, Physical Chemistry in Aerodynamics and Space Flight (Pergamon Press, New York, 1961), p. 228.

these plots tell us little about the parameter σ alone.

For Ar, we compare in Fig. 17 the Morse potentials corresponding to the E_n with the Morse potential due to KH, Abrahamson's TFD¹⁹ potential, and potentials deduced from high energy scattering experiments by Berry,²¹ AJ,²² AM,²³ and AJB.²⁴ (The curve labeled Kihara BFS will be discussed presently.) The agreement is rather good between the Morse potentials and the scattering potentials. Particularly noteworthy is the agreement between the most recently determined scattering potentials^{22,24} and the Morse potential corresponding to the E_1 and E_2 minimization. For N_2 , we see in Fig. 18 that all of the Morse potentials shown give good agreement with the scattering potential deduced from scattering experiments by Amdur, Mason and Jordan²⁵ (AMJ) and its extrapolation to small separations. For CH_4 , Kr, and Xe the Morse potentials determined here are seen in Figs. 19-21 to give slightly better agreement with scattering potentials²⁶⁻²⁸ than do those based on crystal properties.² In Fig. 20 we also

21. H. W. Berry, Phys. Rev. 99, 553 (1955).

22. I. Amdur and J. E. Jordan, private communication 24 November 1964: $\varphi(r) = 155.4/r^{5.48}$ e.v., $1.6 < r < 1.9$ Å; $\varphi(r) = 197.6/r^{6.12}$ e.v., $1.9 < r < 2.2$ Å.

23. I. Amdur and E. A. Mason, J. Chem. Phys. 22, 670 (1954).

24. I. Amdur, J. E. Jordan and R. R. Bertrand, Proceedings of the IIIrd International Conference on the Physics of Electronic and Atomic Collisions, 1963, (North Holland Press, Amsterdam).

25. I. Amdur, E. A. Mason, and J. E. Jordan, J. Chem. Phys. 27, 527 (1957).

26. I. Amdur, M. S. Longmire and E. A. Mason, J. Chem. Phys. 35, 895 (1961).

27. I. Amdur and E. A. Mason, J. Chem. Phys. 23, 2268 (1955).

28. I. Amdur and E. A. Mason, J. Chem. Phys. 25, 624 (1956).

show the (exp-6) potential for Kr determined by Mason²⁹ from various gas properties. Our Morse potential gives slightly better agreement with the scattering potential while the (exp-6) potential gives better agreement with the TFD potential.¹⁹ For Ne, it is seen that none of the Morse potentials give particularly good agreement with either the TFD potential¹⁹ or the scattering potentials due to Berry³⁰ and AM.³¹ It appears that c/σ is somewhat too large for any of our potentials while that ratio is somewhat too small for the KH potential.

In summary, we note first that in a number of cases our potentials appear to agree better with the scattering and TFD potentials than do the Morse potentials determined by KH.² The latter are usually too "soft", as might have been expected, since they are based largely on low-temperature properties. Secondly, we see that for a single substance the differences between the various potentials suggested in Table II are usually too small for the scattering potentials to be used to provide a definitive choice among them. Overall these comparisons do not show any of our Morse potentials to be grossly incorrect,³² nor do they provide any clue as to why they allow no better agreement

29. E. A. Mason, J. Chem. Phys. 32, 1832 (1960).

30. H. W. Berry, Phys. Rev. 75, 913 (1949).

31. I. Amdur and E. A. Mason, J. Chem. Phys. 23, 415 (1955).

32. Abrahamson (Ref. 19) has compared the experimental scattering potentials as well as his own TFD potentials with extrapolations of a number of other model potentials. With respect to the latter he found the modified Buckingham (exp.6) potential to give order-of-magnitude and frequently closer agreement with experiment, while the Lennard-Jones (12-6) potentials generally rise quite rapidly with decreasing r to values exceeding the experimental ones by several 100 per cent.

with the experimental viscosity than that we have found.

We list in Table III a "most likely" set of Morse potential parameters selected on the basis of the arguments given in the previous sections. They are based almost entirely on the results of the E_1 and E_2 fitting procedures. We consider the potential for Ne not to be well determined by our method. Although we term the remaining potentials to be at least conditionally well determined, they do not permit a description even of the data from which they were derived within the estimated experimental error. Thus, the three-parameter Morse function, like all other models so far considered, appears to be insufficiently flexible (and insufficiently realistic) to account accurately for a wide range of experimental data.³³

It is of some interest to compare our results for Ar with those recently obtained by BFS⁸ in terms of the Kihara potential³⁴

$$\begin{aligned}\varphi(r) &= \infty, \quad r^* \leq \gamma \\ &= 4\epsilon \left[\left(\frac{1-\gamma}{r^*-\gamma} \right)^{12} - \left(\frac{1-\gamma}{r^*-\gamma} \right)^6 \right], \quad r^* > \gamma.\end{aligned}$$

33. Even so, a knowledge of even these poor approximations are, and will continue for sometime to be, of interest for use in estimating properties which are not readily available from experiment. Indeed, it is largely because of their possible use in high temperature applications that we have dwelt so long on an examination of the high energy region.

34. T. Kihara, Rev. Mod. Phys. 25, 839 (1953).

TABLE III
COMPARISON OF POTENTIAL FUNCTIONS FOR
SOME SIMPLE NONPOLAR SUBSTANCES

Substance	ϵ/k ($^{\circ}\text{K}$)	σ \AA	r_m \AA	Source
Ar	132.6	3.546	4.031	a
	142.9	3.363	3.735	b
	147.2	3.314	3.677	c
	137.5	3.165	3.812	d
N_2	120.3	3.717	4.208	a
	139.2	3.526	3.736	c
CH_4	221.8	3.507	3.943	a
	204.3	3.620	3.991	c
Kr	199.2	3.563	4.067	a
	215.6	3.521	3.898	c
	191.1	...	4.077	d
	200.0	3.577	4.036	e
Xe	273.1	3.950	4.500	a
	298.8	3.878	4.283	c
	264.4	...	4.438	d
Ne	70.5	2.598	2.848	a, f
	44.3	...	3.130	d

a. "Most likely" Morse potentials. Those potentials determined by minimizing E_1 are weighted most heavily.

b. Kihara potential, Ref. 8.

c. Kihara potential, Ref. 35.

d. Guggenheim and McGlashan potential, Ref. 36.

e. Modified Buckingham (exp-6) potential, Ref. 29.

f. This potential may be grossly in error since it is not well-determined by our method.

Here $r^* = r/\sigma$, γ is the ratio of the core diameter to the collision diameter σ , and ϵ and σ have the same significance as for the Morse potential. By performing simultaneous least-squares fits of $\eta_x(T)/(MT)^{\frac{1}{2}}$ and $B_x(T)$, (a procedure similar to although not entirely equivalent to our own), they fixed the Kihara parameters for Ar to be: $\epsilon/k = 142.9^\circ\text{K}$, $\gamma = 0.1$, and $\sigma = 3.363 \text{ \AA}$. With this set of parameters they obtained perceptibly better agreement between calculated and experimental viscosities and second virial coefficients for Ar than that we found for the Morse potential. For example, their largest percentage error for a single viscosity was about 5 per cent while the root mean square percentage error we obtained for viscosity is about 6 per cent. (As can be seen from Fig. 3 the largest percentage errors are associated with the low-temperature viscosity which is essentially ignored in both the E_1 and the E_2 fitting procedure. The overall percentage error is not appreciably improved when E_3 is minimized.) Furthermore, the largest single deviation found by BFS for $B(T)$ was $-3.6 \text{ cm}^3/\text{mole}$ and their standard deviation was $1.2 \text{ cm}^3/\text{mole}$, while our standard deviation for $B(T)$ is about $3.7 \text{ cm}^3/\text{mole}$. By these measures, their Kihara potential for Ar clearly gives a better fit of both $B(T)$ and $\eta(T)$ than does our "most likely" Morse function. Although for neither potential is the agreement within estimated experimental error (ca. 1-2 per cent for viscosity), on the basis of these results the Kihara potential must be considered, at least provisionally, the more realistic of the two.

Unfortunately, the form which makes the Kihara potential so

intuitively appealing for the description of two-body phenomena at low-to-moderate temperatures becomes less and less realistic for high energy applications. This aspect is depicted in Fig. 17 where the Kihara potential for Ar (determined by BFS) is compared with the potentials we have previously discussed. There it is seen that even outside its hard repulsive core, the Kihara potential, like the Lennard-Jones (12-6) potential on which it is based, predicts too hard a repulsion.³²

Recently, Sherwood and Prausnitz³⁵ (SP) fixed the Kihara potential parameters for a number of substances we consider by comparing with $B(T)$ data alone. Their procedure is not expected to fix as realistic a potential as does the BFS procedure in view of our early discussion. However, the fairly good agreement between the SP and BFS potentials for Ar makes it seem worthwhile to extend the comparison between our Morse potentials and the Kihara potentials to include the SP results in Table III. For the rare gases we may further extend this comparison to include the results of Guggenheim and McGlashan³⁶ who determined their potentials almost entirely from crystal properties. (BFS showed that the Guggenheim and McGlashan potential for Ar gives less satisfactory agreement with the viscosity than does the Kihara potential.)

35. A. E. Sherwood and J. M. Prausnitz, J. Chem. Phys. 41, 429 (1964).

36. E. A. Guggenheim and M. L. McGlashan, Proc. Roy. Soc. (London) A255, 456 (1960); Mol. Phys. 3, 563 (1960).

In Fig. 23 we show the attractive region of three model potentials for Ar: the Kihara potential determined by BFS, the Guggenheim and McGlashan potential³⁶ (the dashed portions are drawn free-hand), and our "most likely" Morse potential. It is evident that they disagree in a number of respects. We have included in Table III one of the possible Buckingham (exp-6) potentials (φ_B) for Kr suggested by Mason²⁹ mainly on the basis of a comparison with thermal diffusion and $\eta(T)$ data. The agreement with our "most likely" Morse potential (φ_M) is striking. We have already seen in Fig. 20 that these two potentials agree quite well in the repulsive region. In Fig. 24 we see that the two are quite similar in the attractive region as well: φ_B has a steeper repulsive limb and a slower long range decay than does φ_M .

Considering their diverse forms, and the diverse methods used to fix them, the agreement between the various models is relatively good. There is little question, however, that the investigation of more flexible and more realistic models is justified. In our opinion a corresponding effort must be expended in devising improved methods of deducing the features of the potentials from experiment.

Acknowledgments

Our thanks go to Mrs. Carol Monash for her painstaking programming assistance. We are grateful to Professor I. Amdur for making available to us unpublished potentials for the Ar-Ar system, to Dr. J. A. Barker for providing us some of his unpublished calculations on the Kihara potential, and to Dr. L. A. K. Staveley for providing a compilation of experimental second virial coefficient data for a number of substances.

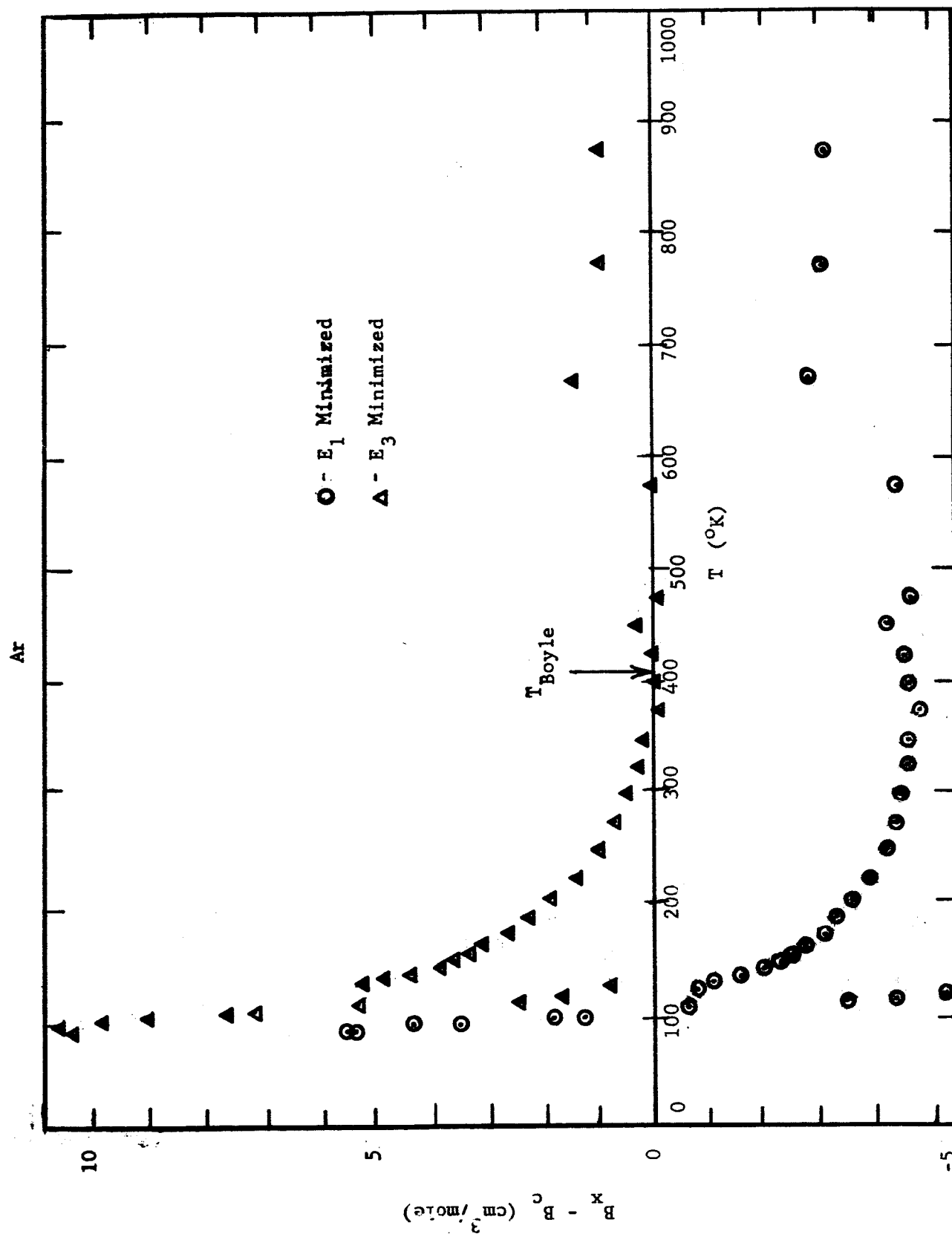


Fig. 1

Comparison of Experimental and Calculated $B(T)$ for Ar

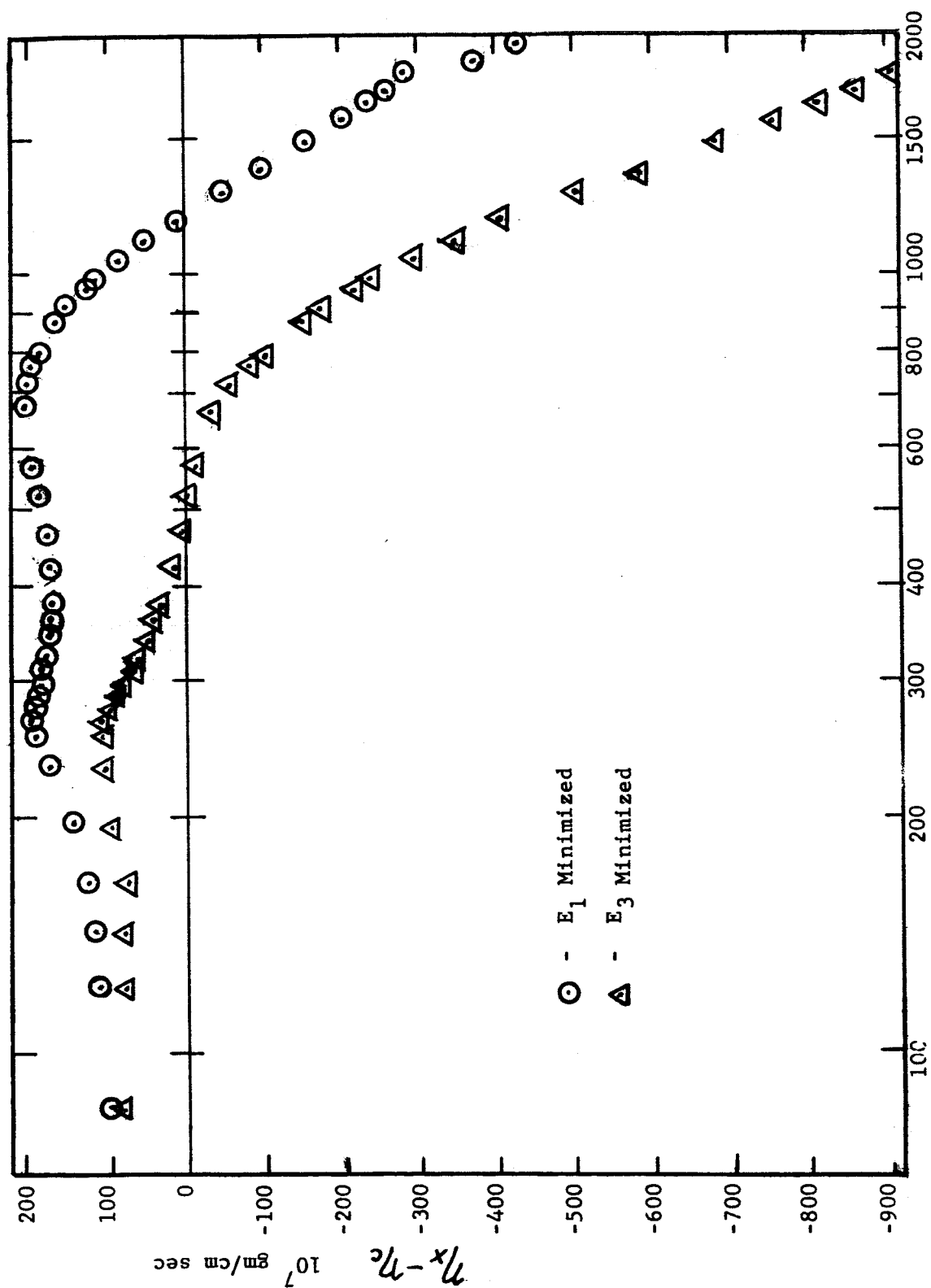


Fig. 2

Comparison of Experimental and Calculated $\eta(T)$ for Ar

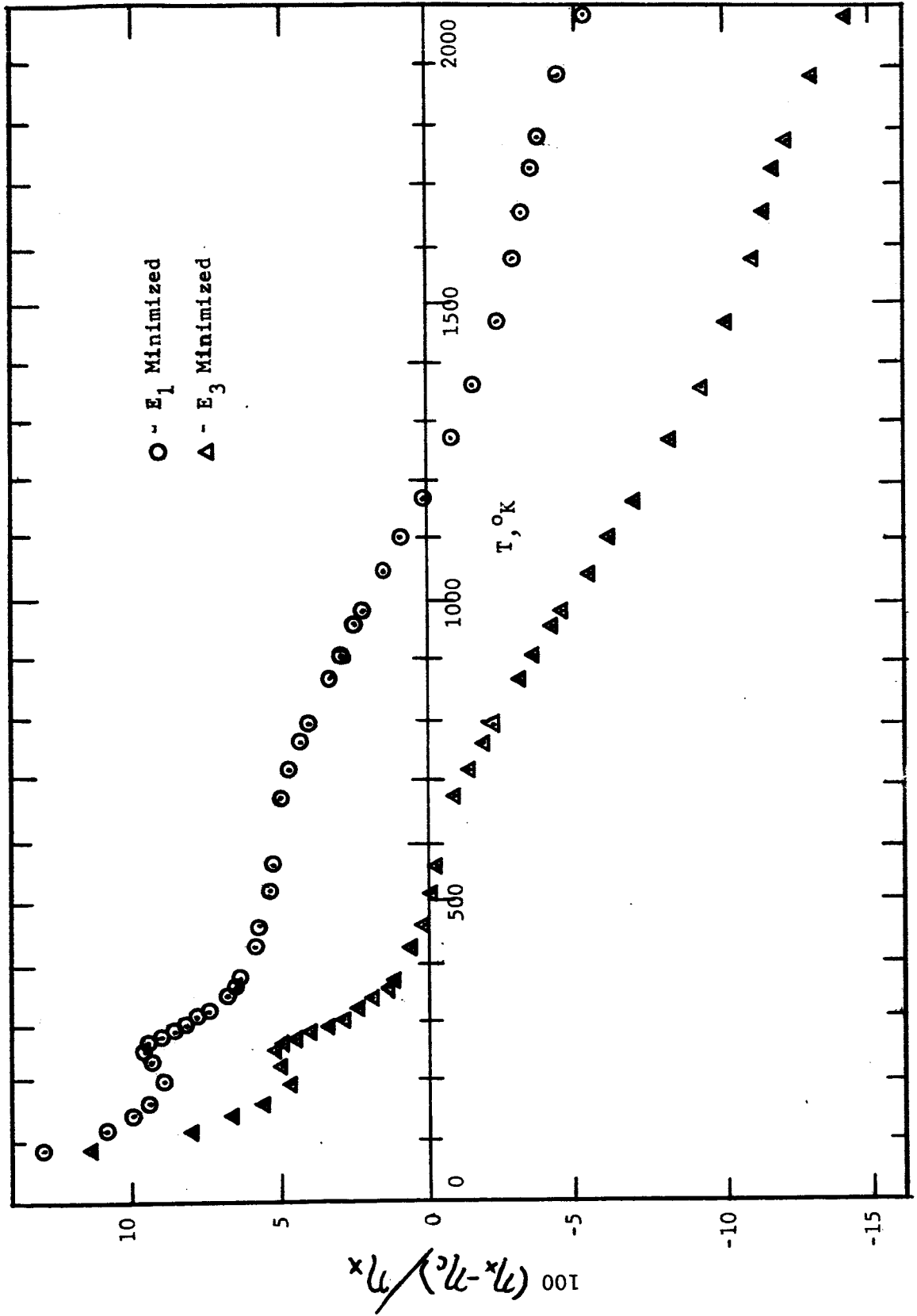


Fig. 3
Percentage Error in Calculated $\eta(T)$ for Ar

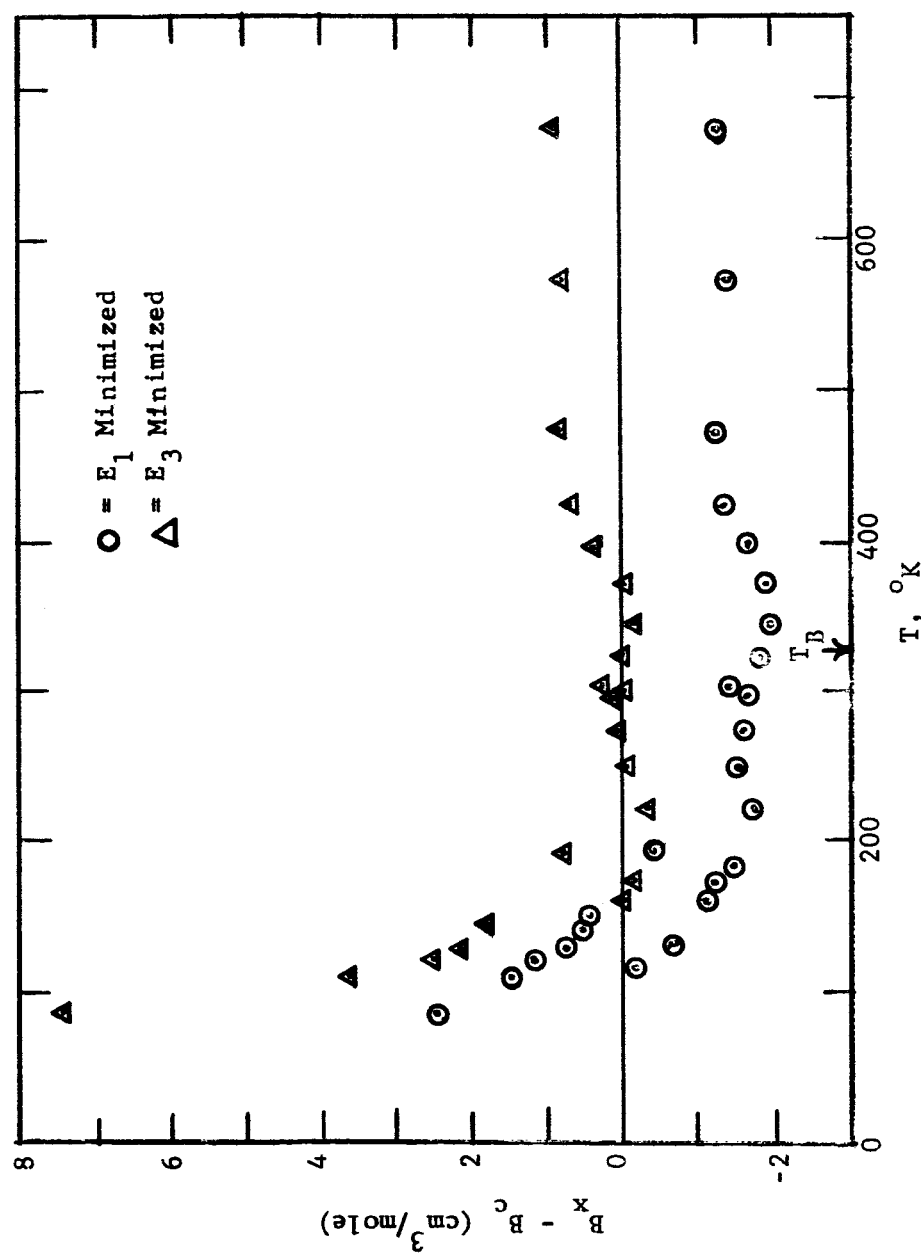


Fig. 4

Comparison of Experimental and Calculated $B(T)$ for N_2

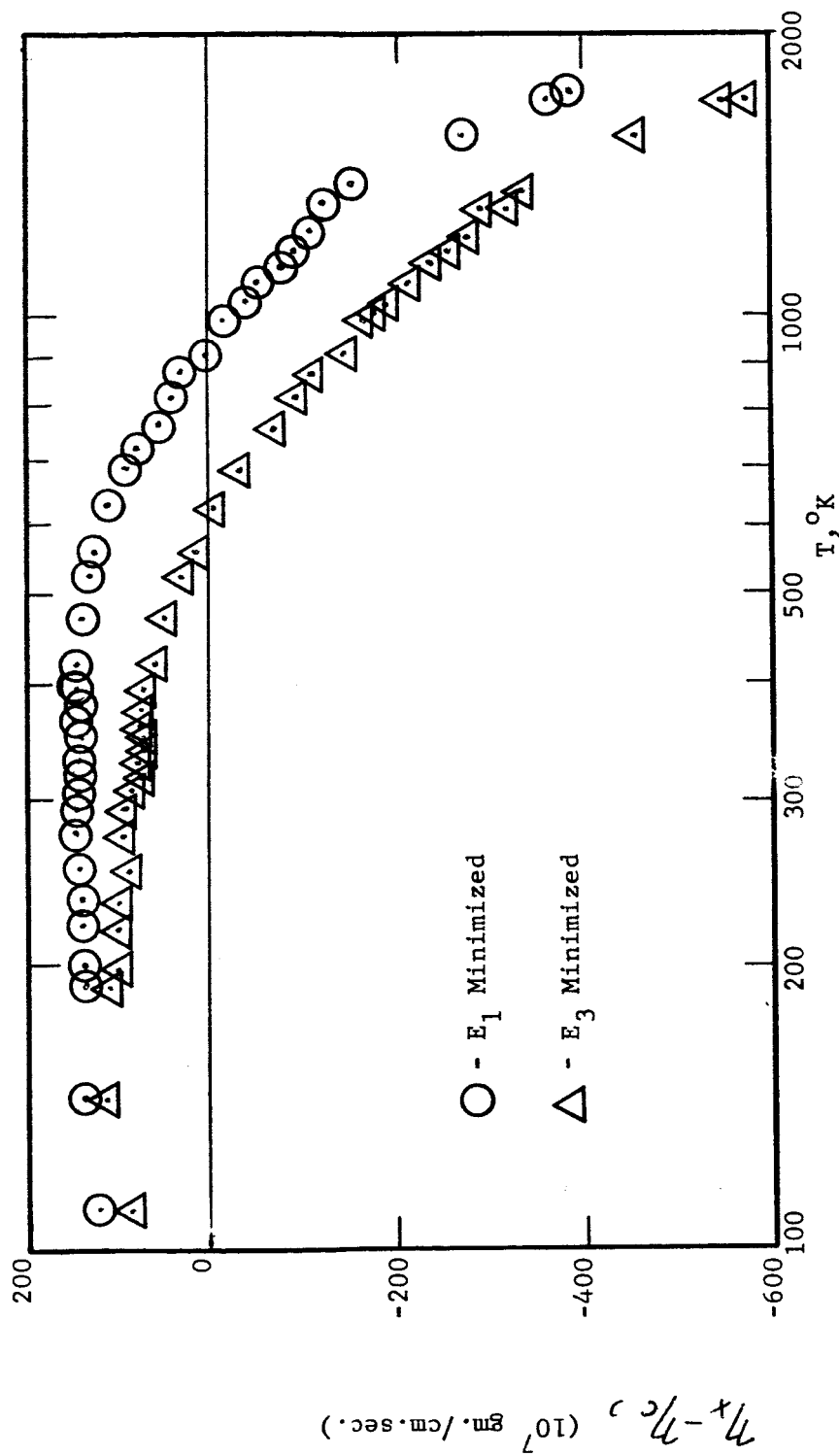


Fig. 5
Comparison of Experimental and Calculated $\eta(T)$ for N_2

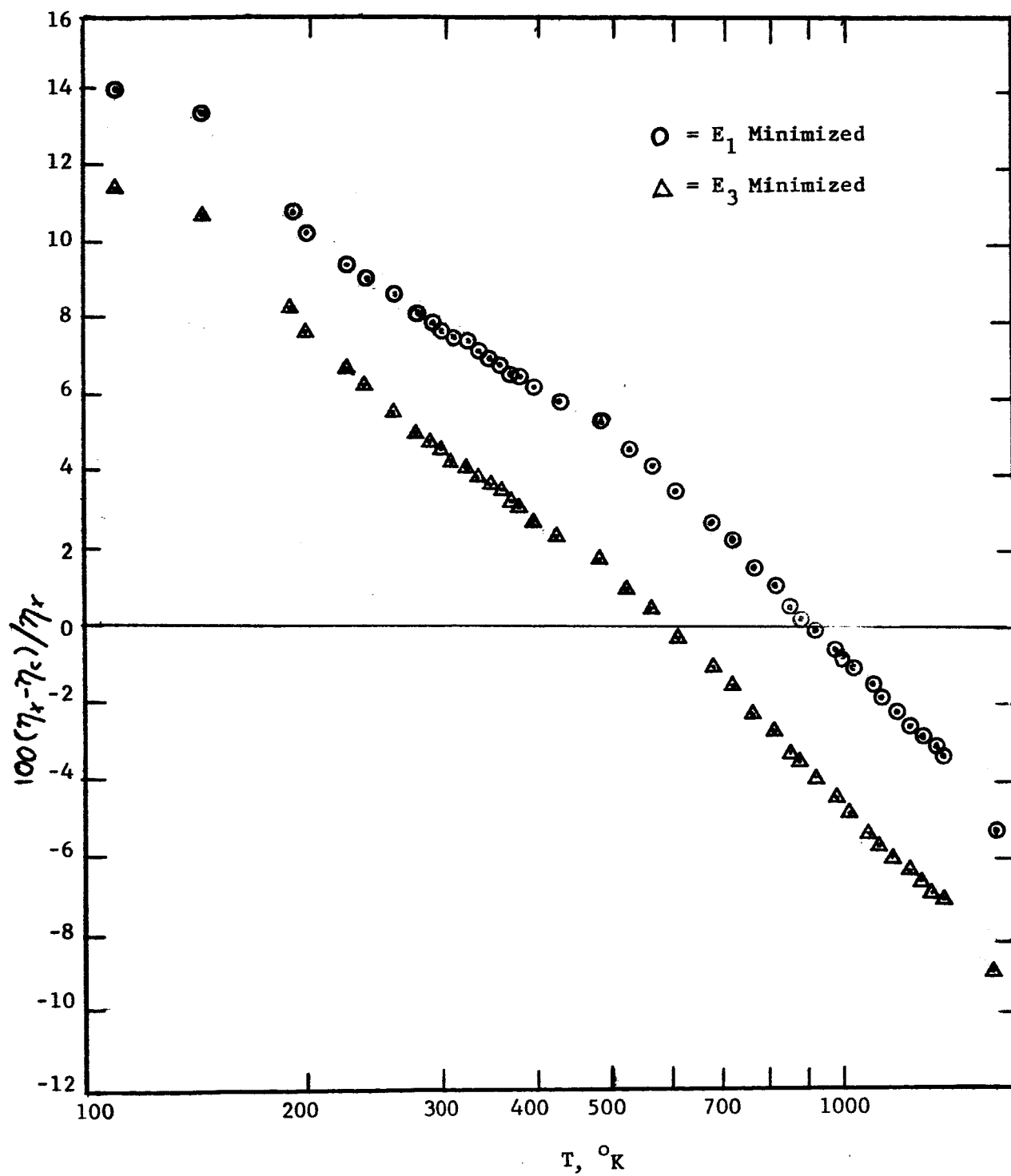


Fig. 6

Percentage Error in Calculated $\eta(T)$ for N_2

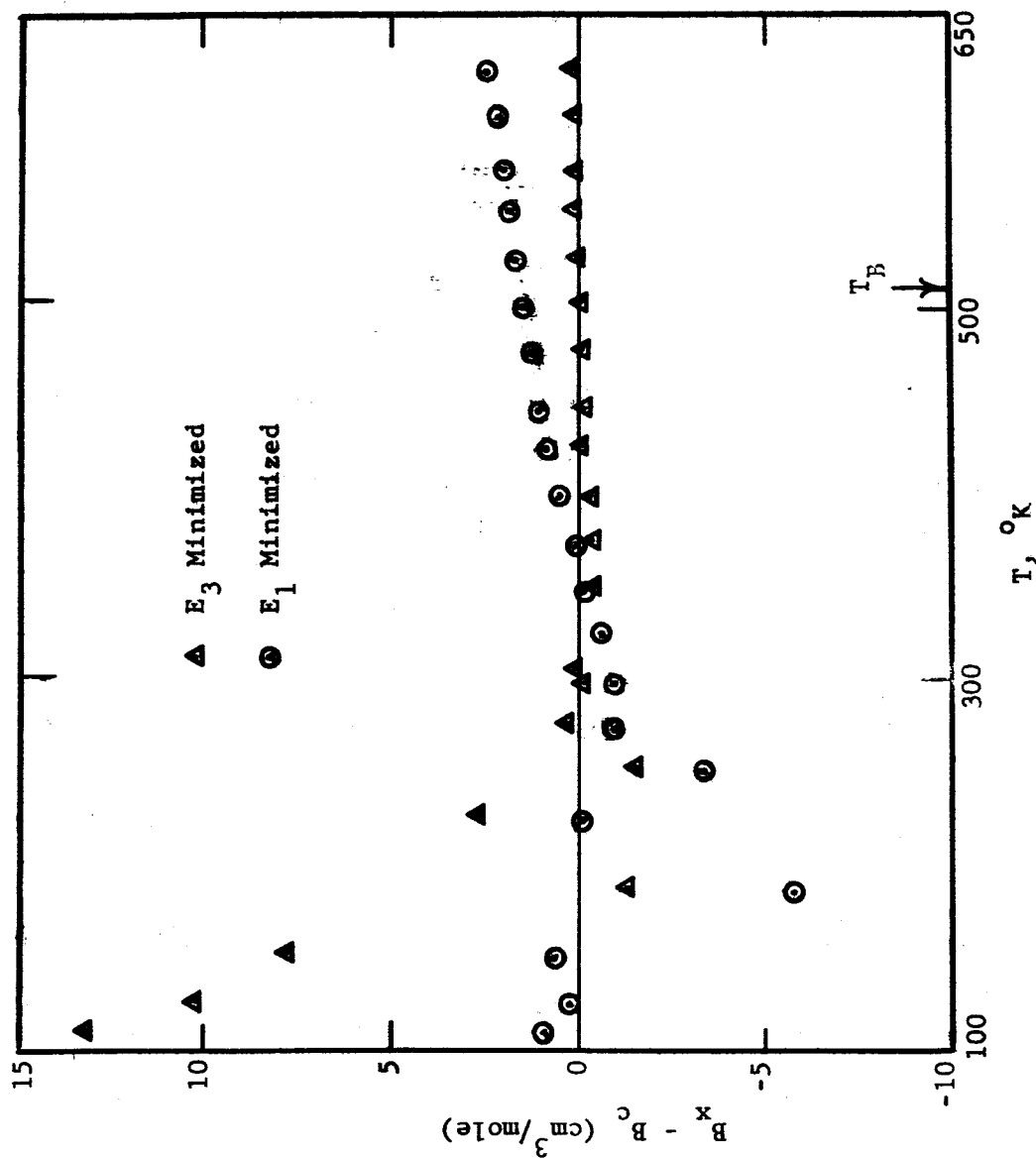


Fig. 7

Comparison of Experimental and Calculated $B(T)$ for CH_4

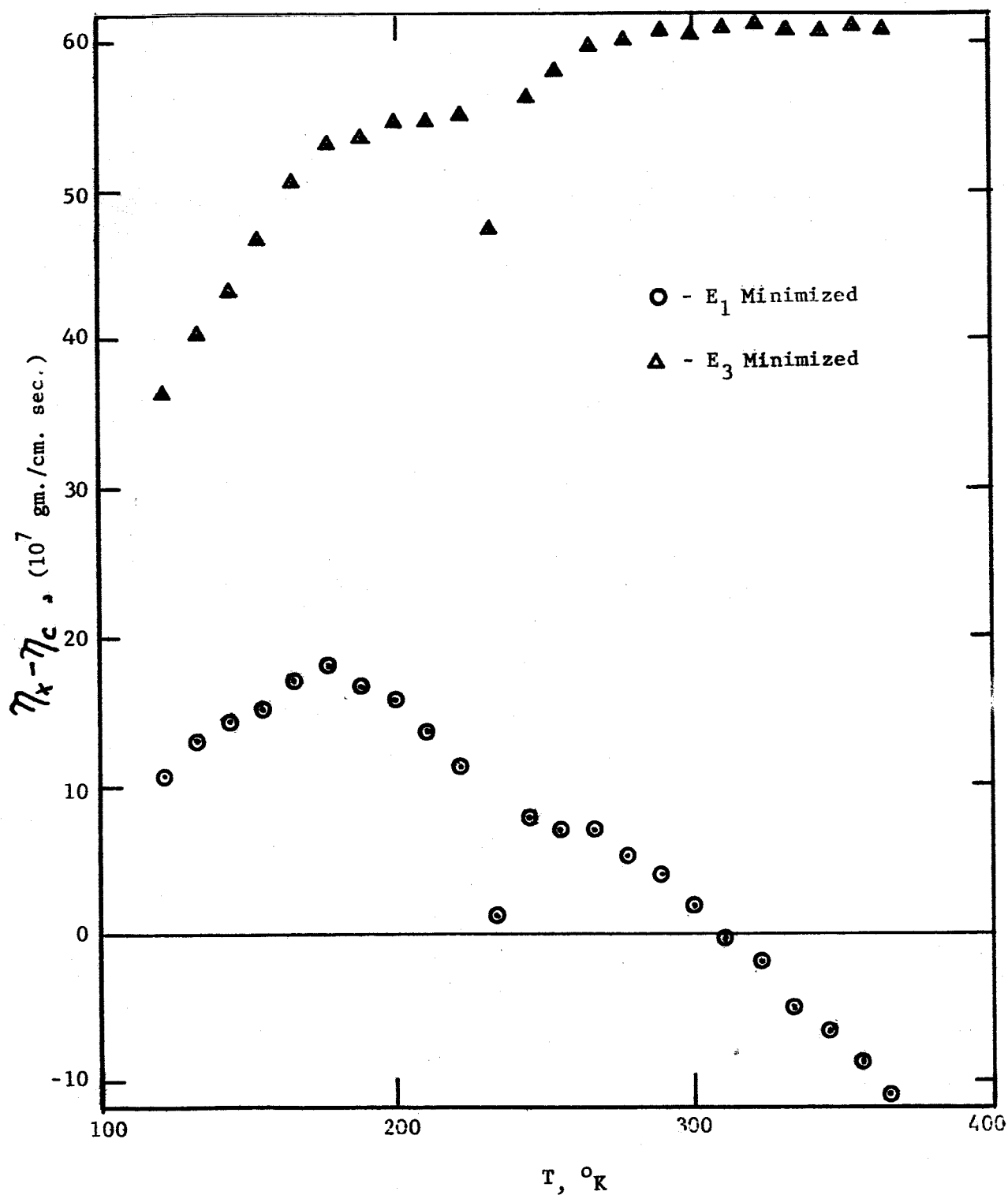


Fig. 8
Comparison of Experimental and Calculated $\eta(T)$ for CH_4

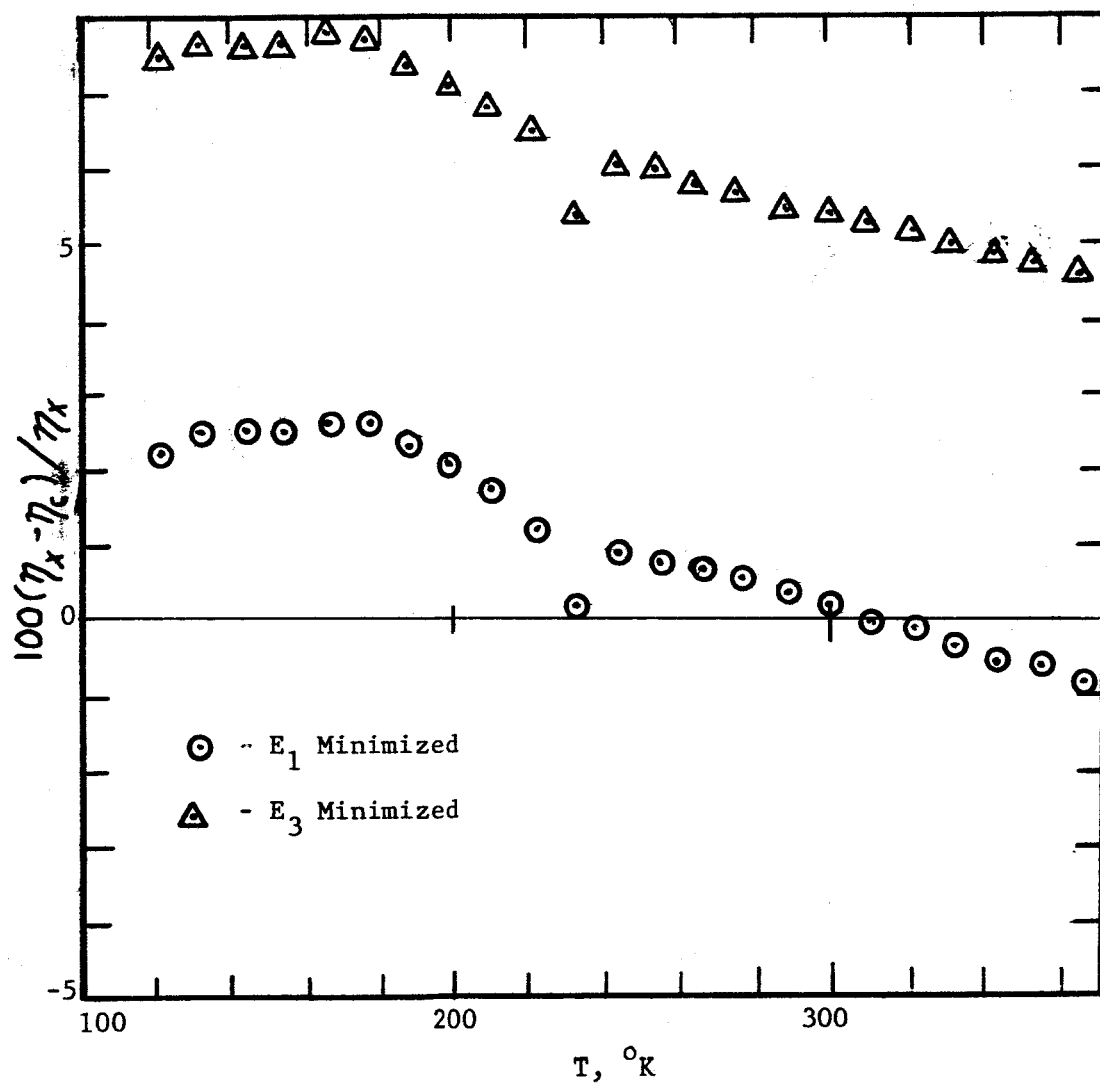


Fig. 9
 Percentage Error in Calculated $\eta(T)$ for CH_4

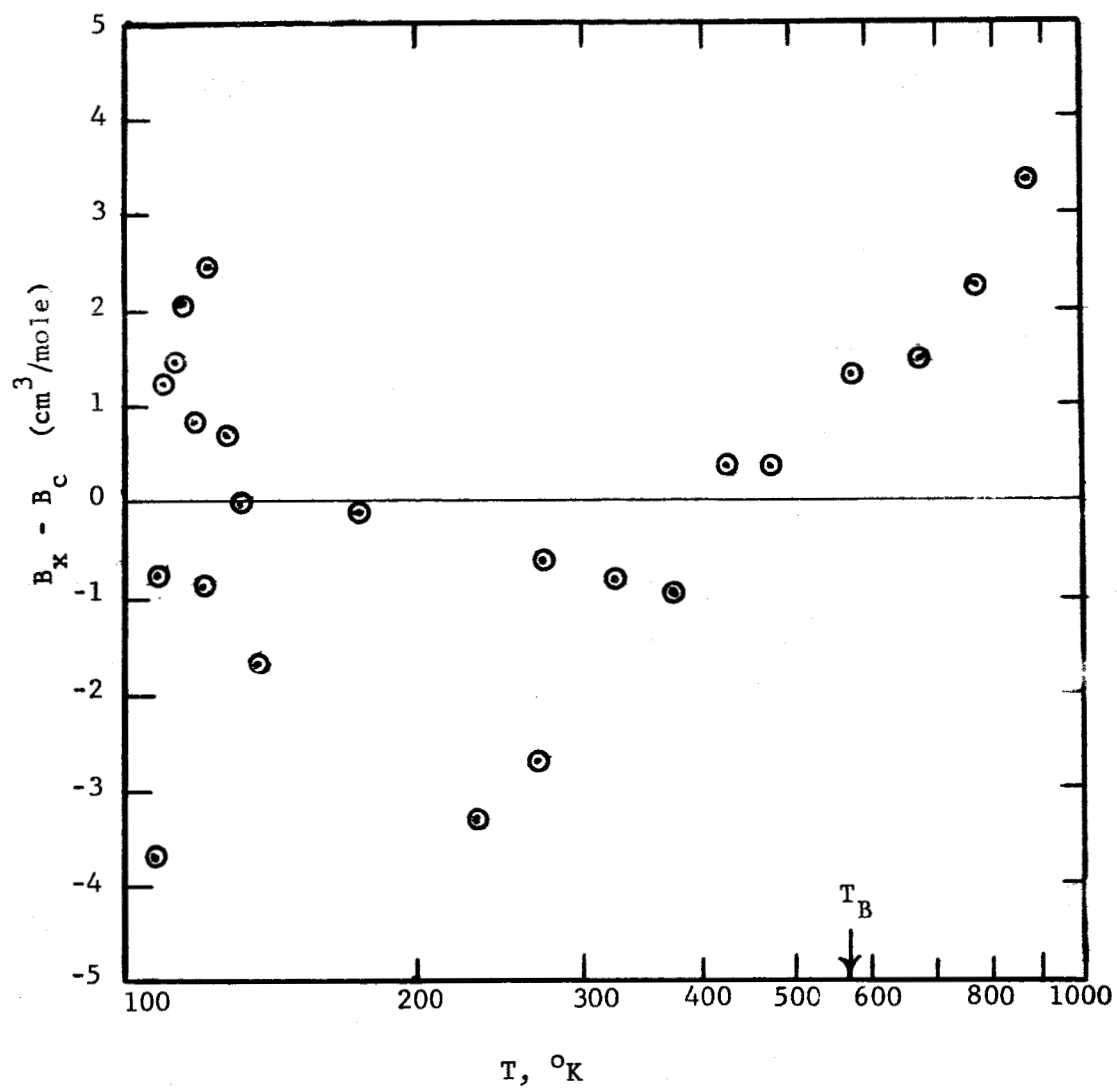


Fig. 10

Comparison of Experimental and Calculated $B(T)$ for Kr

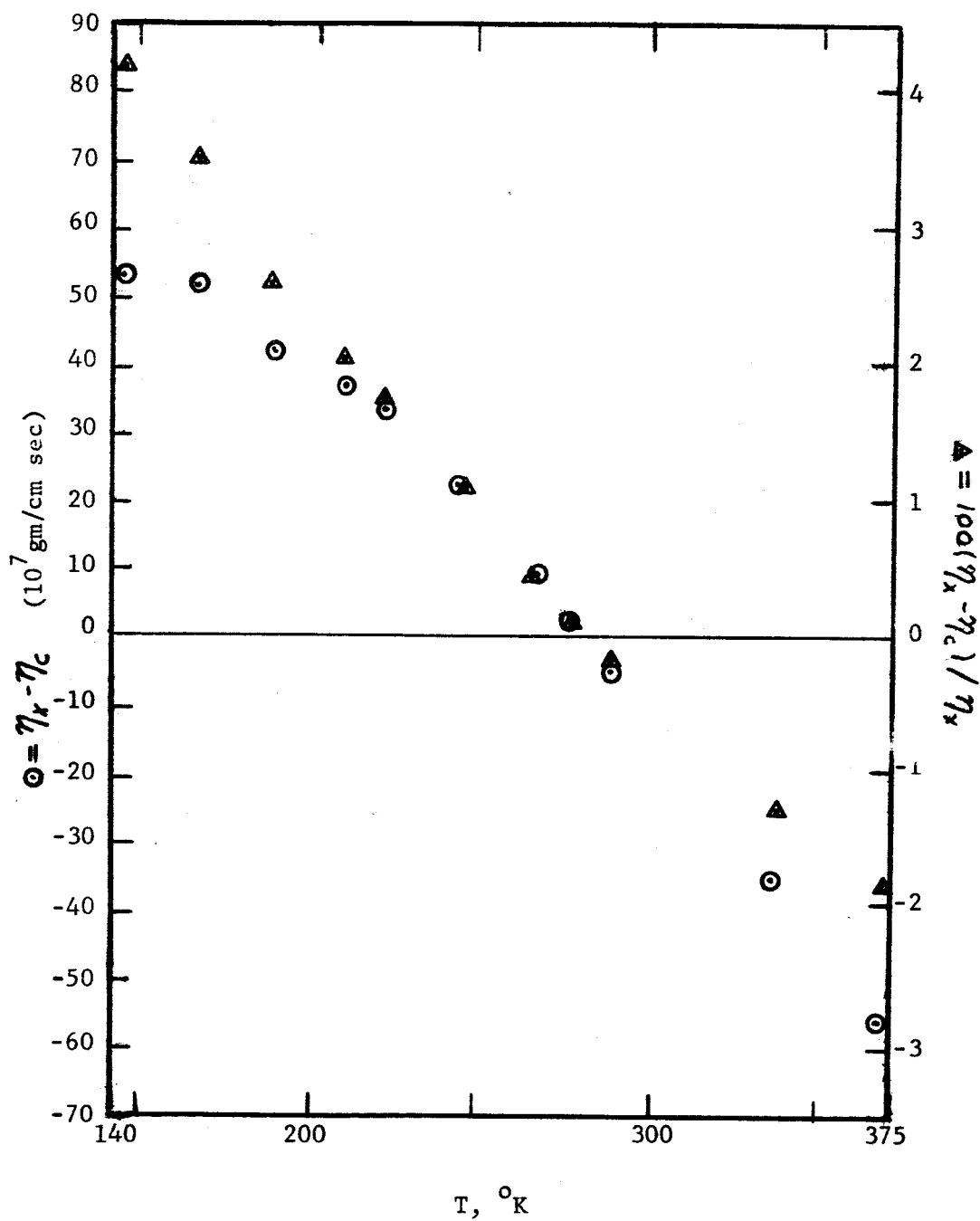
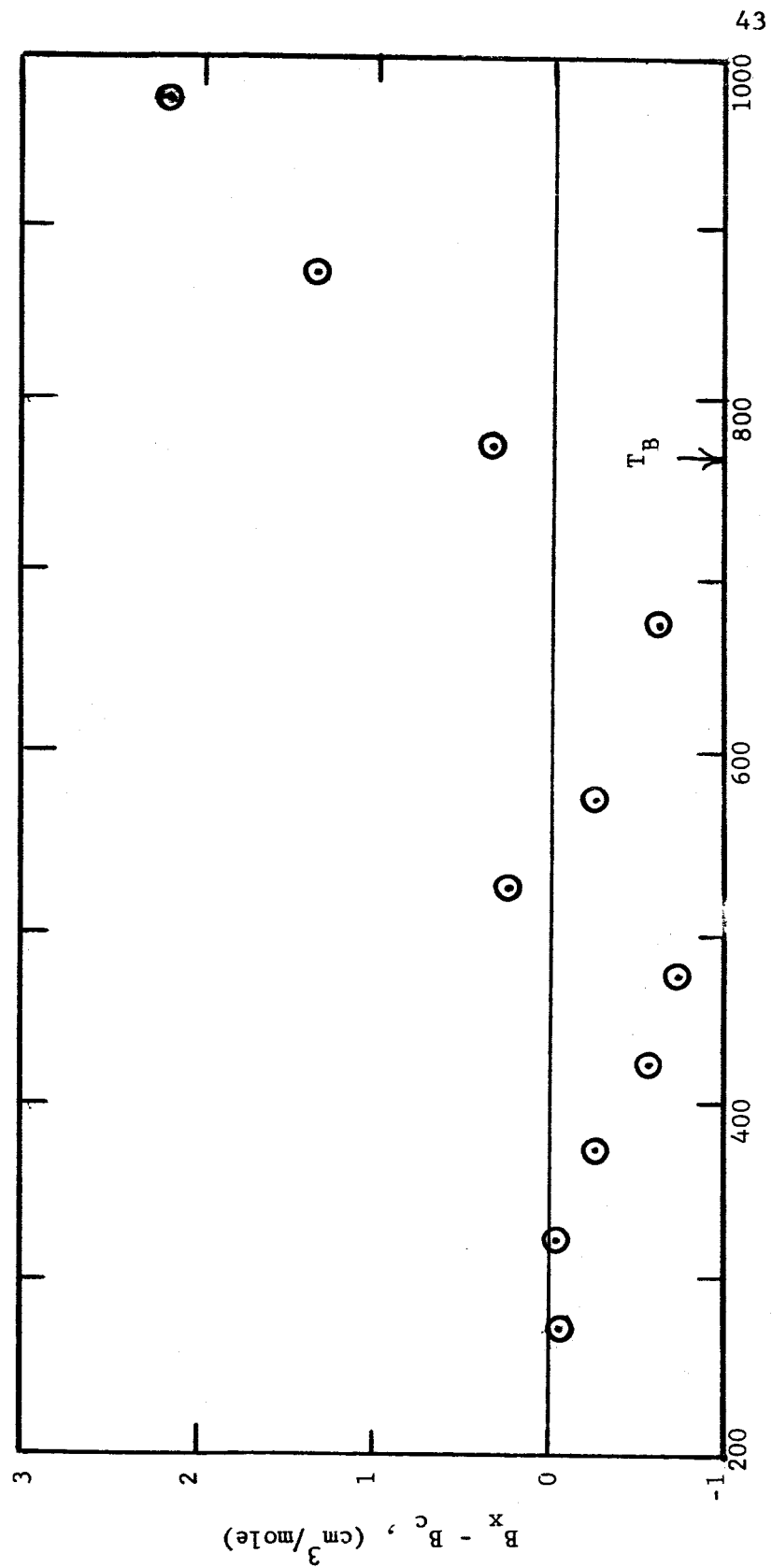


Fig. 11

Absolute and Percentage Errors in the Calculated
 $\eta(T)$ for Kr



$T, ^\circ K$

Fig. 12

Comparison of Experimental and Calculated $B(T)$ for Xe

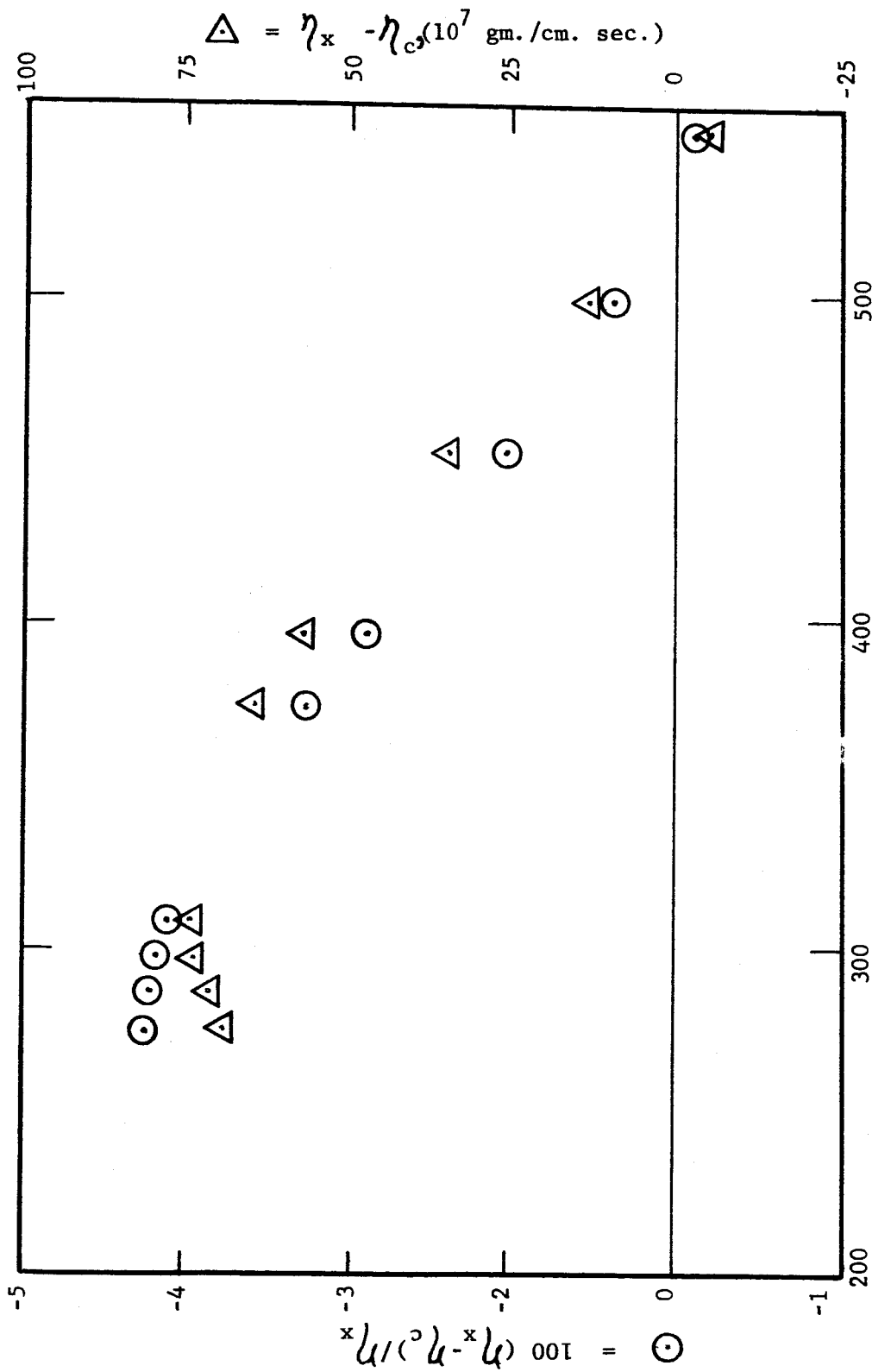


Fig. 13
Absolute and Percentage Errors in the Calculated $\eta(T)$ for Xe

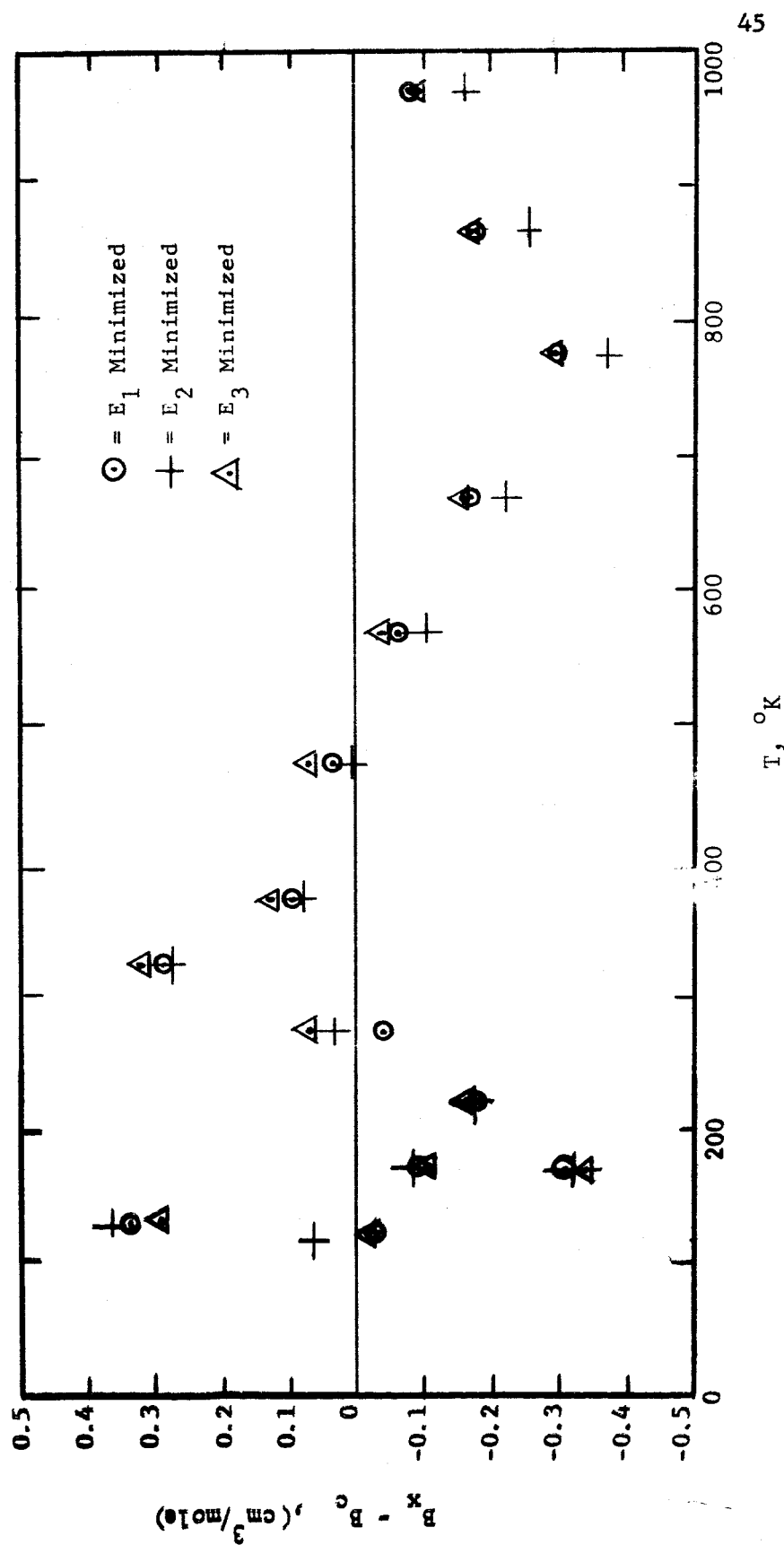


Fig. 14
Comparison of Experimental and Calculated $B(T)$ for Ne

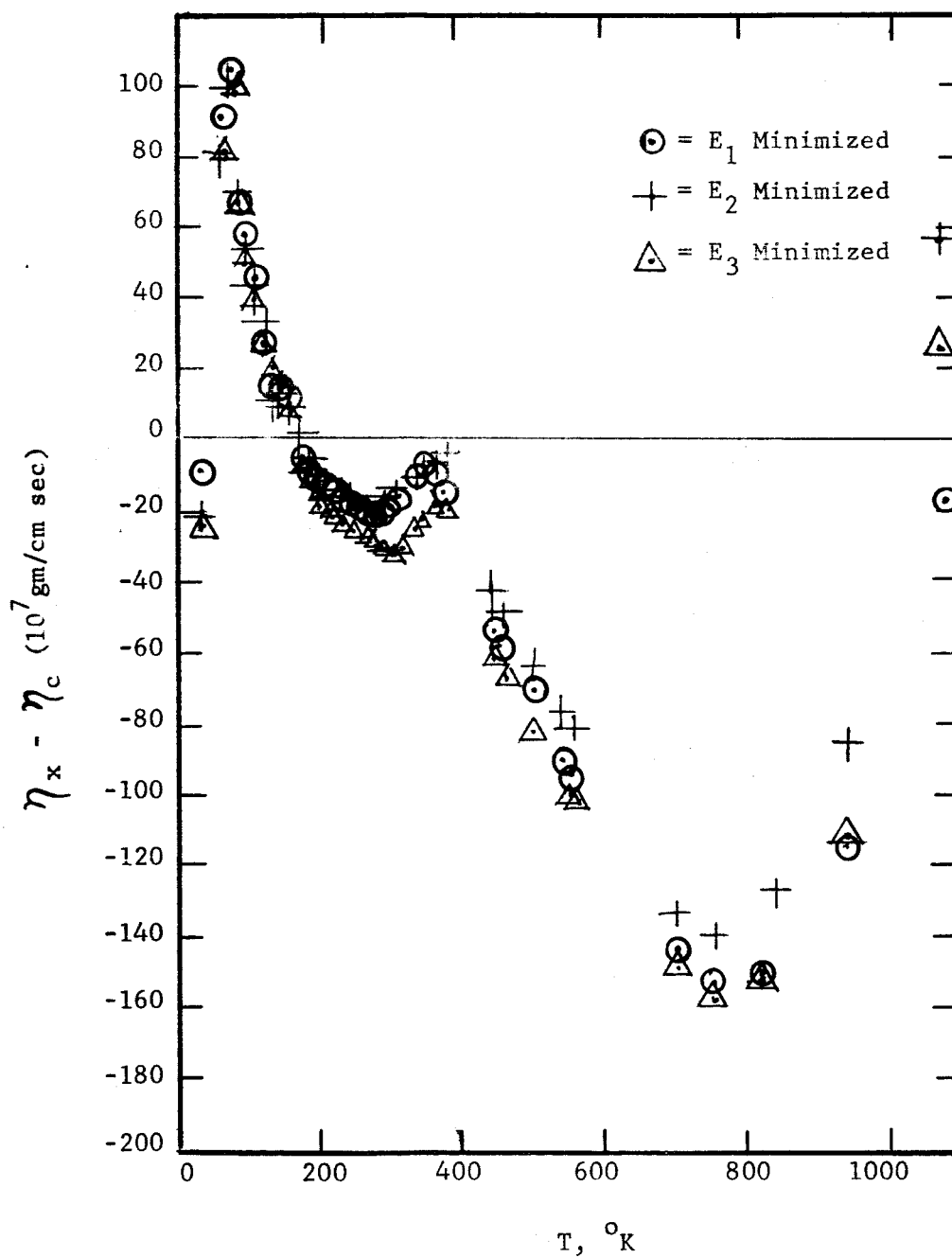


Fig. 15

Comparison of Experimental and Calculated $\eta(T)$ for Ne

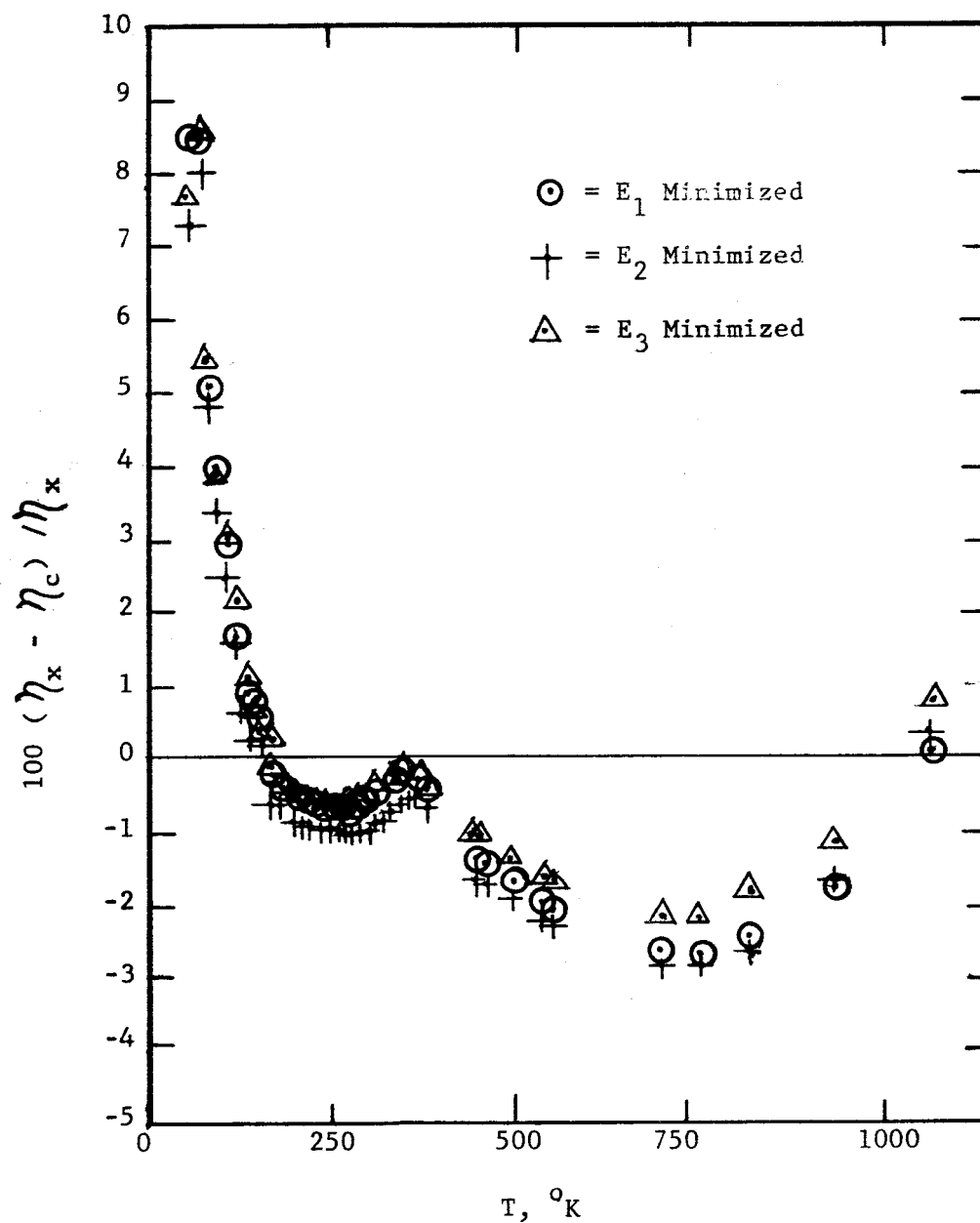


Fig. 16

Percentage Error in Calculated $\eta(T)$ for Ne

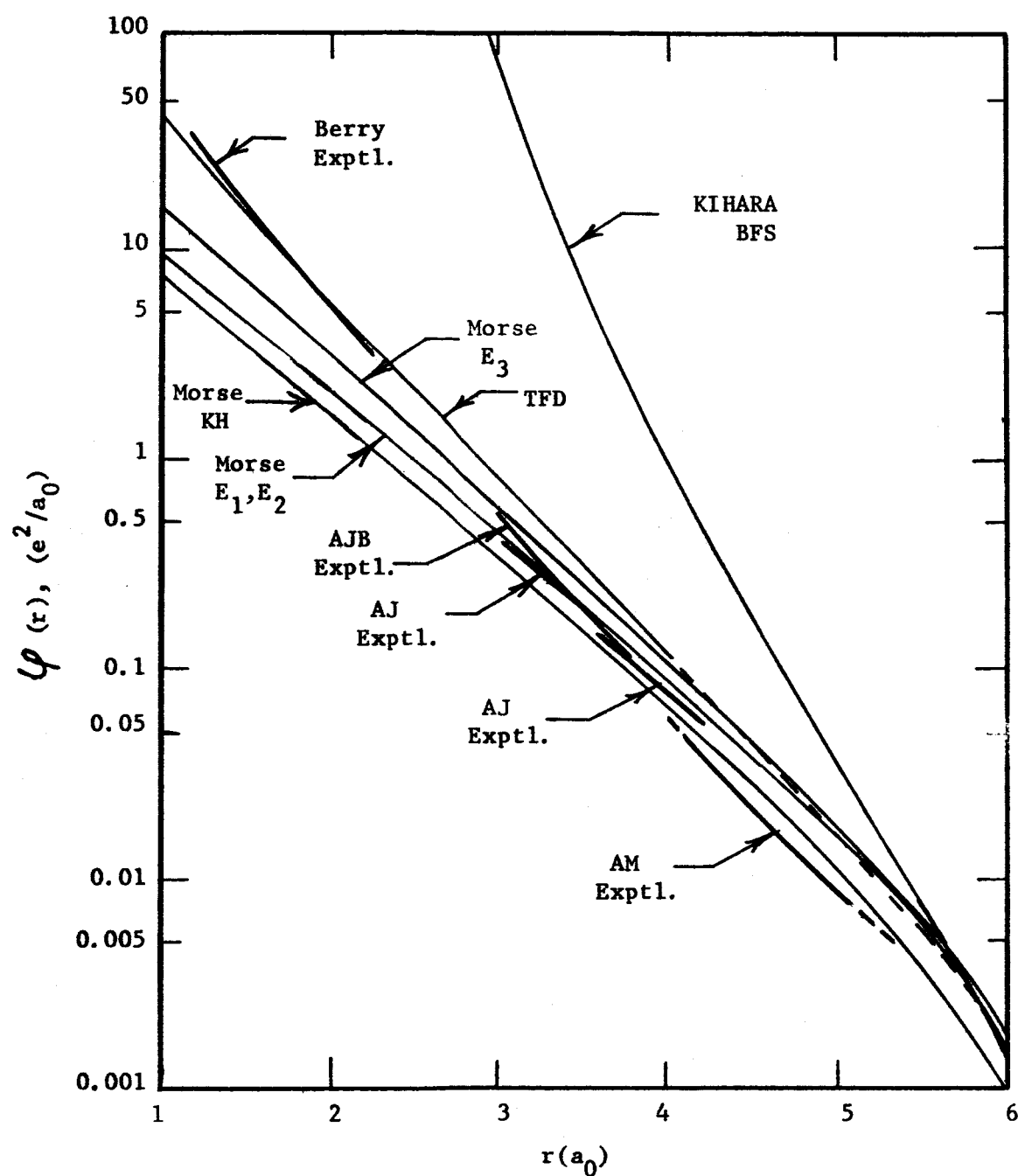


Fig. 17

Repulsive Potentials for Ar-Ar Interactions

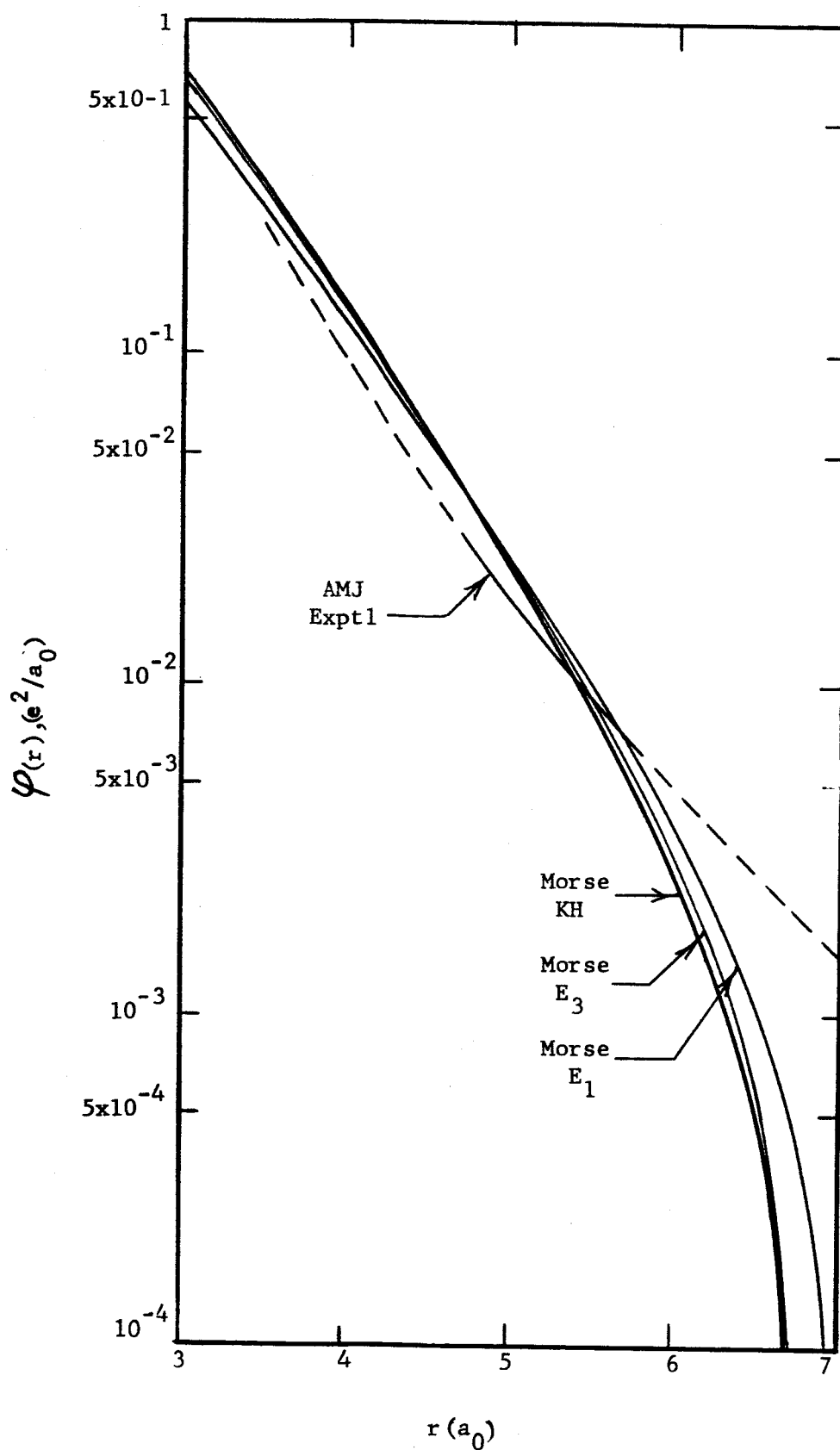


Fig. 18
Repulsive Potentials for $N_2 - N_2$ Interactions

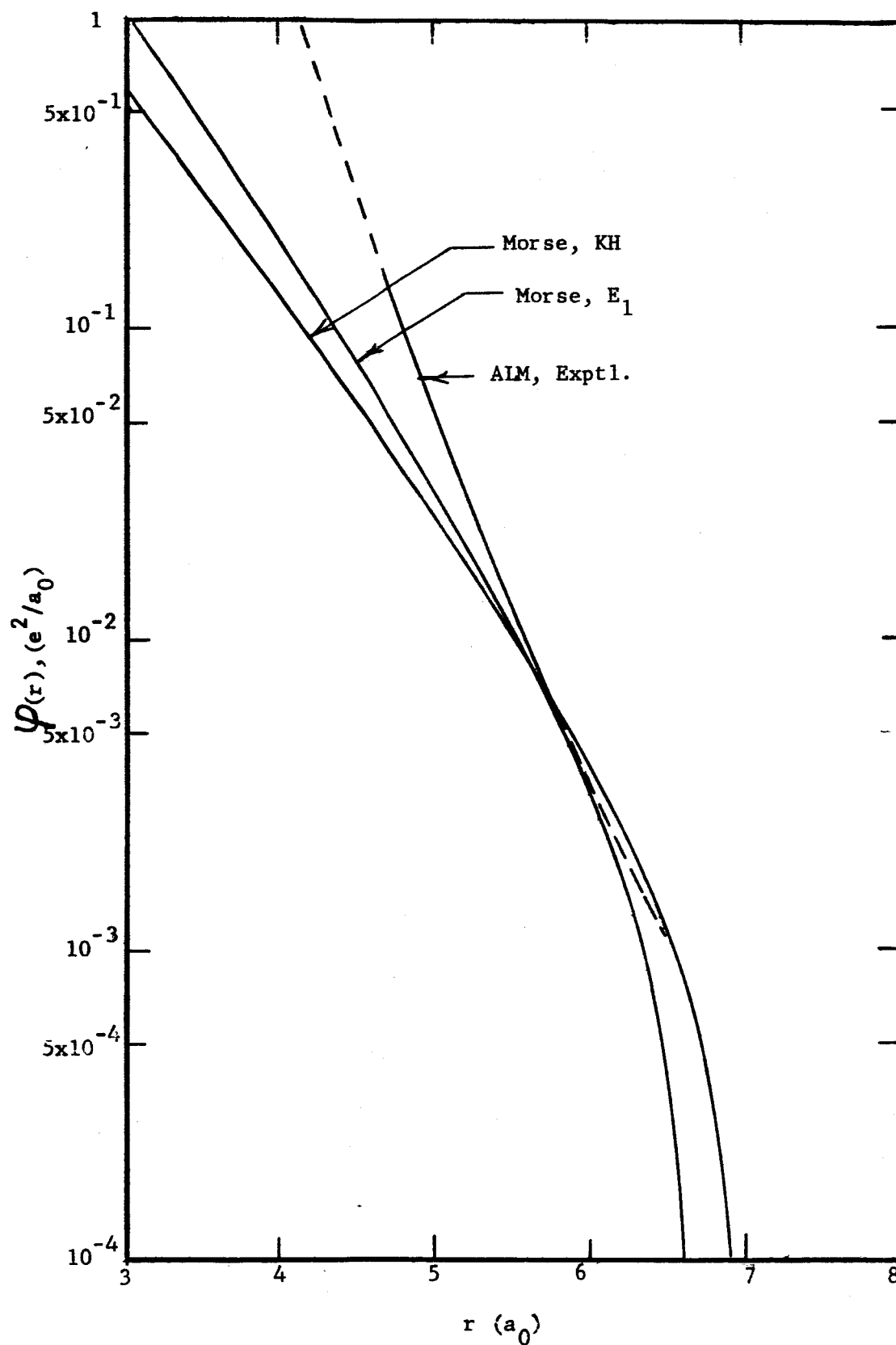


Fig. 19

Repulsive Potentials for $\text{CH}_4 - \text{CH}_4$ Interactions

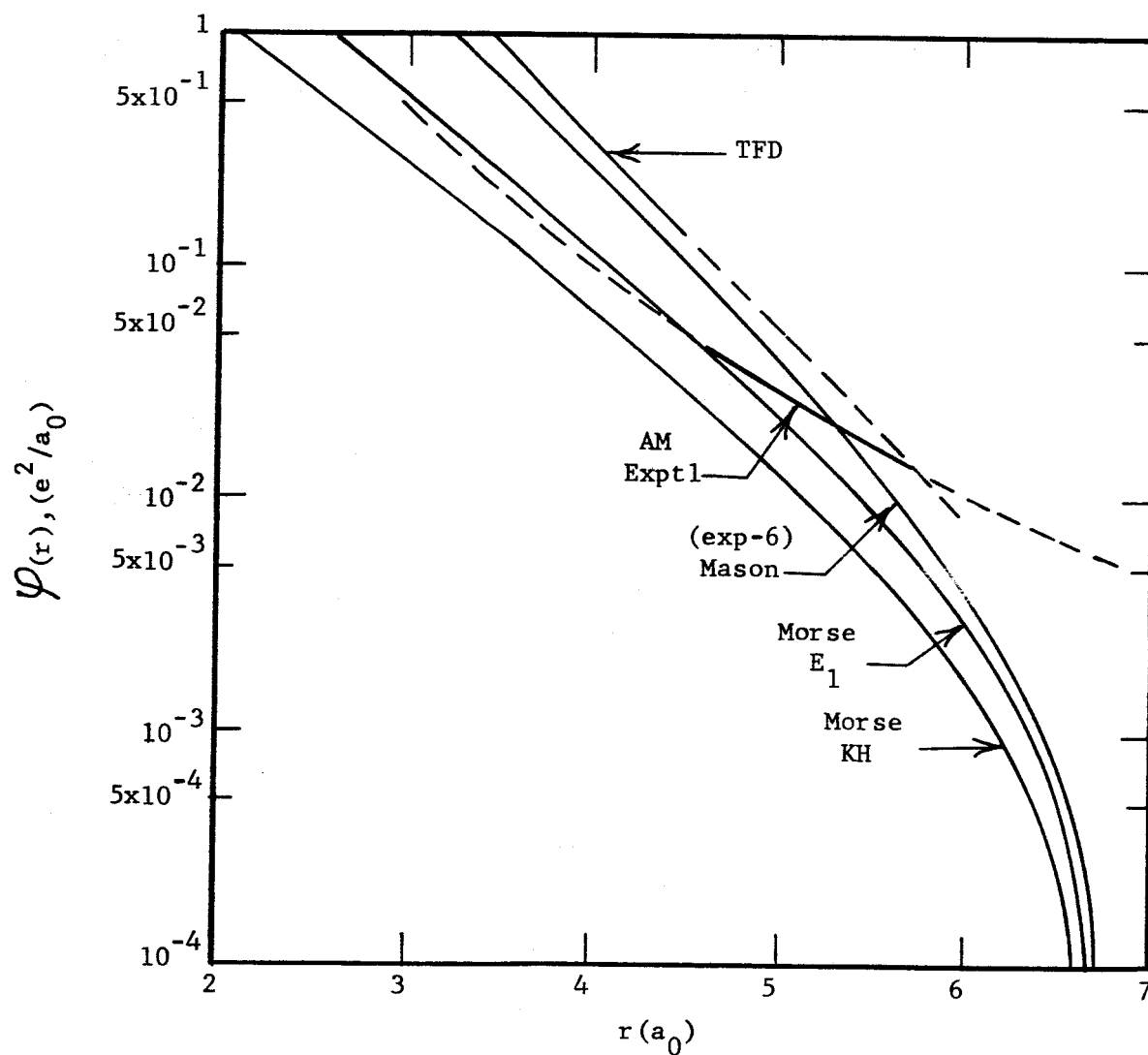


Fig. 20

Repulsive Potentials for Kr-Kr Interactions

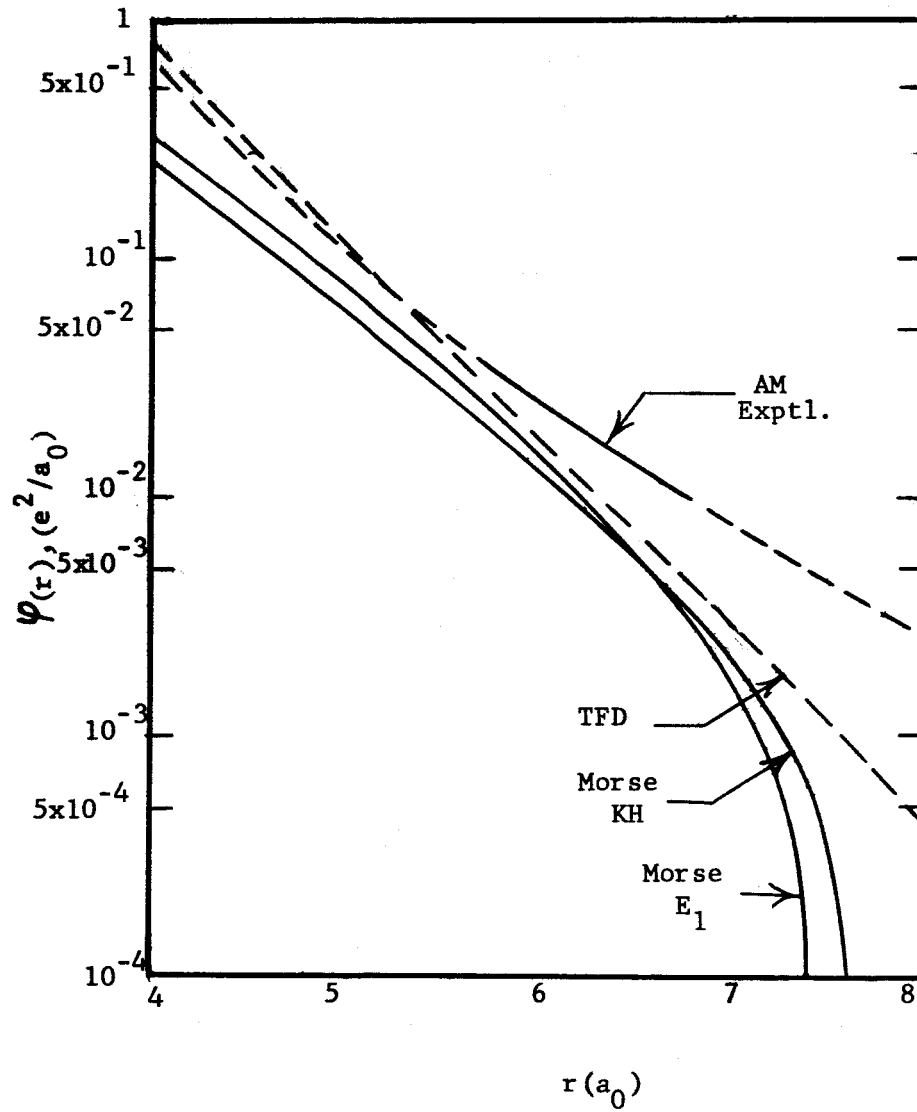


Fig. 21

Repulsive Potentials for Xe - Xe Interactions

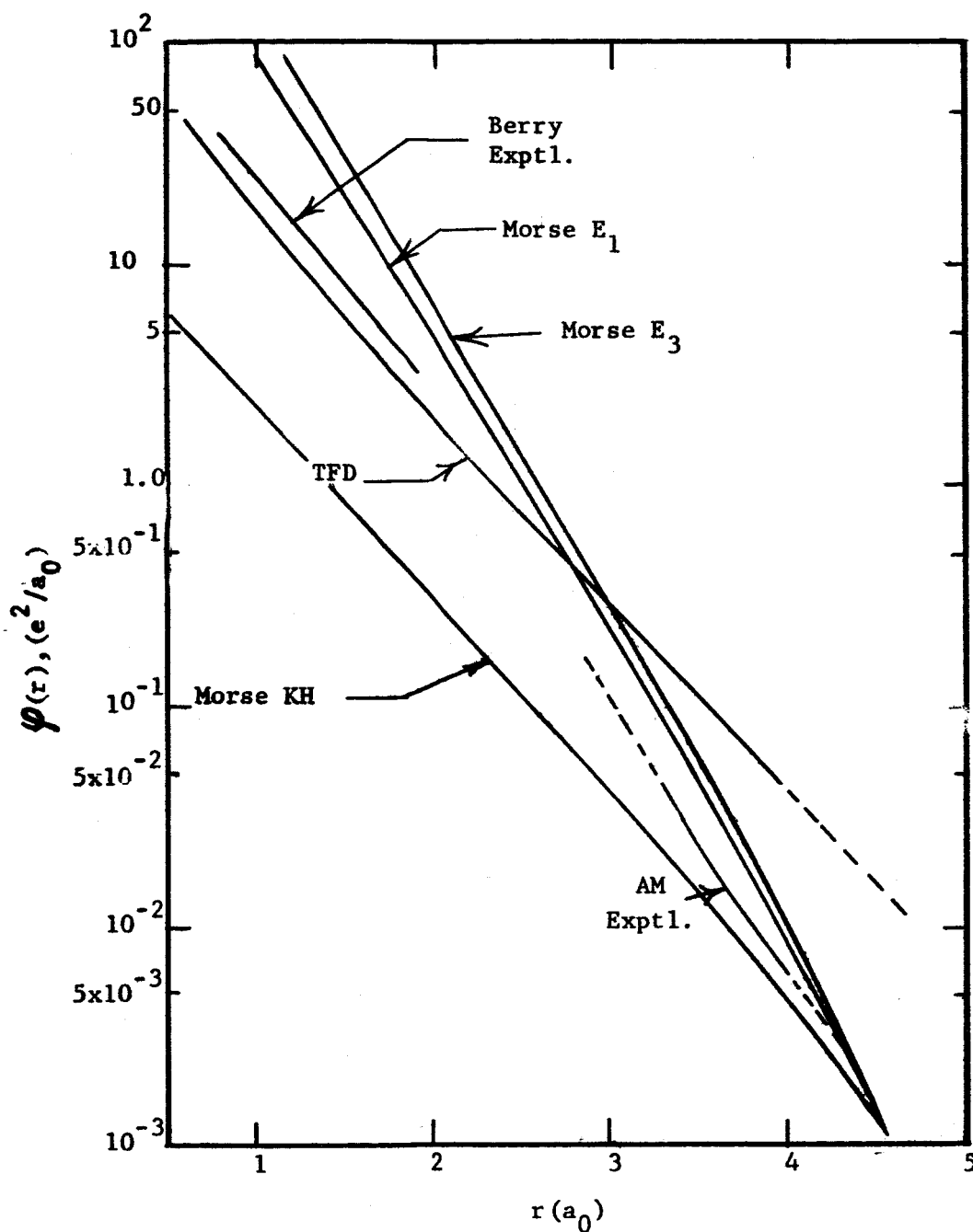


Fig. 22

Repulsive Potentials for Ne-Ne Interactions

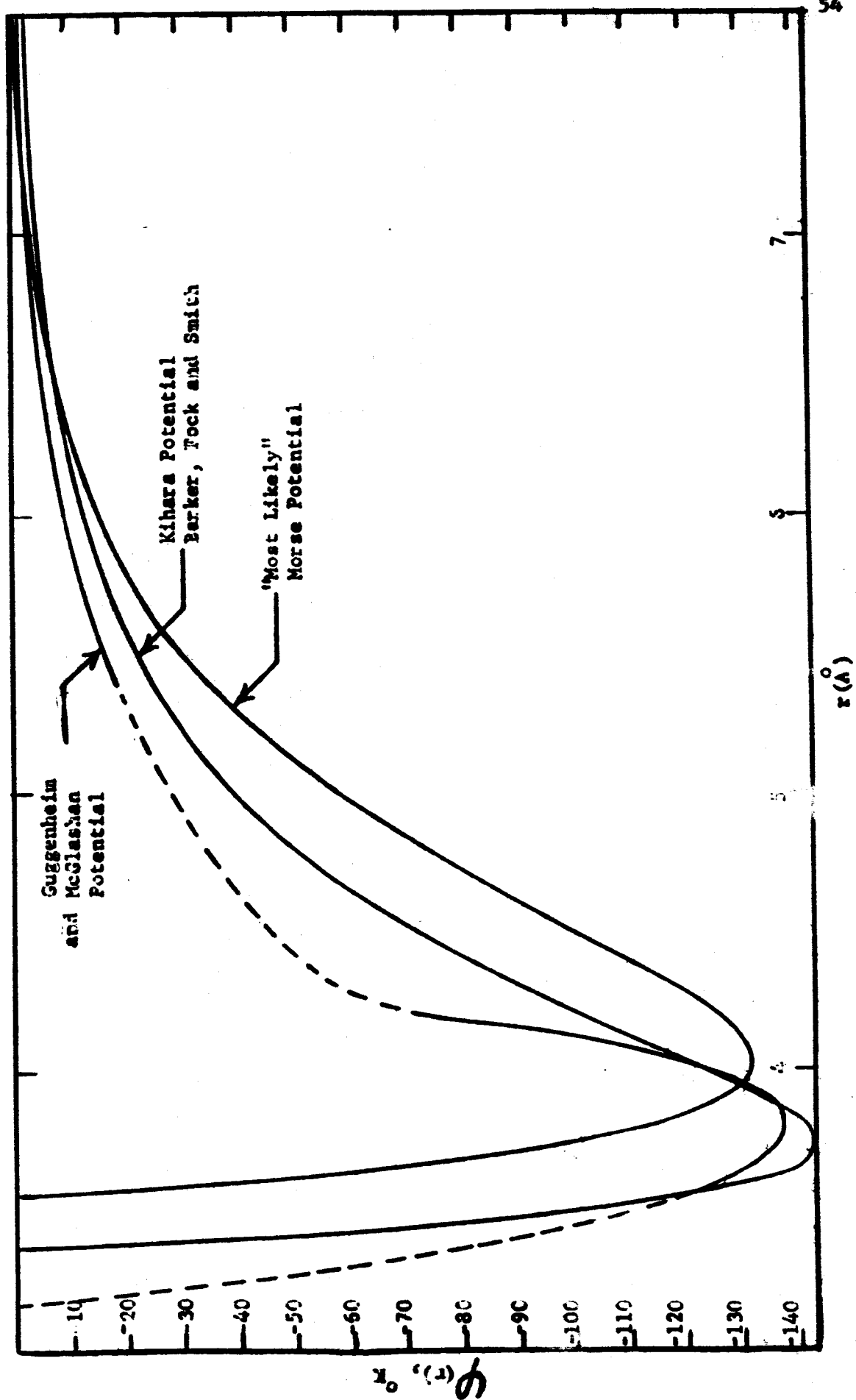


Fig. 23
A Comparison of the Attractive Potentials for Ar-Ar Interactions

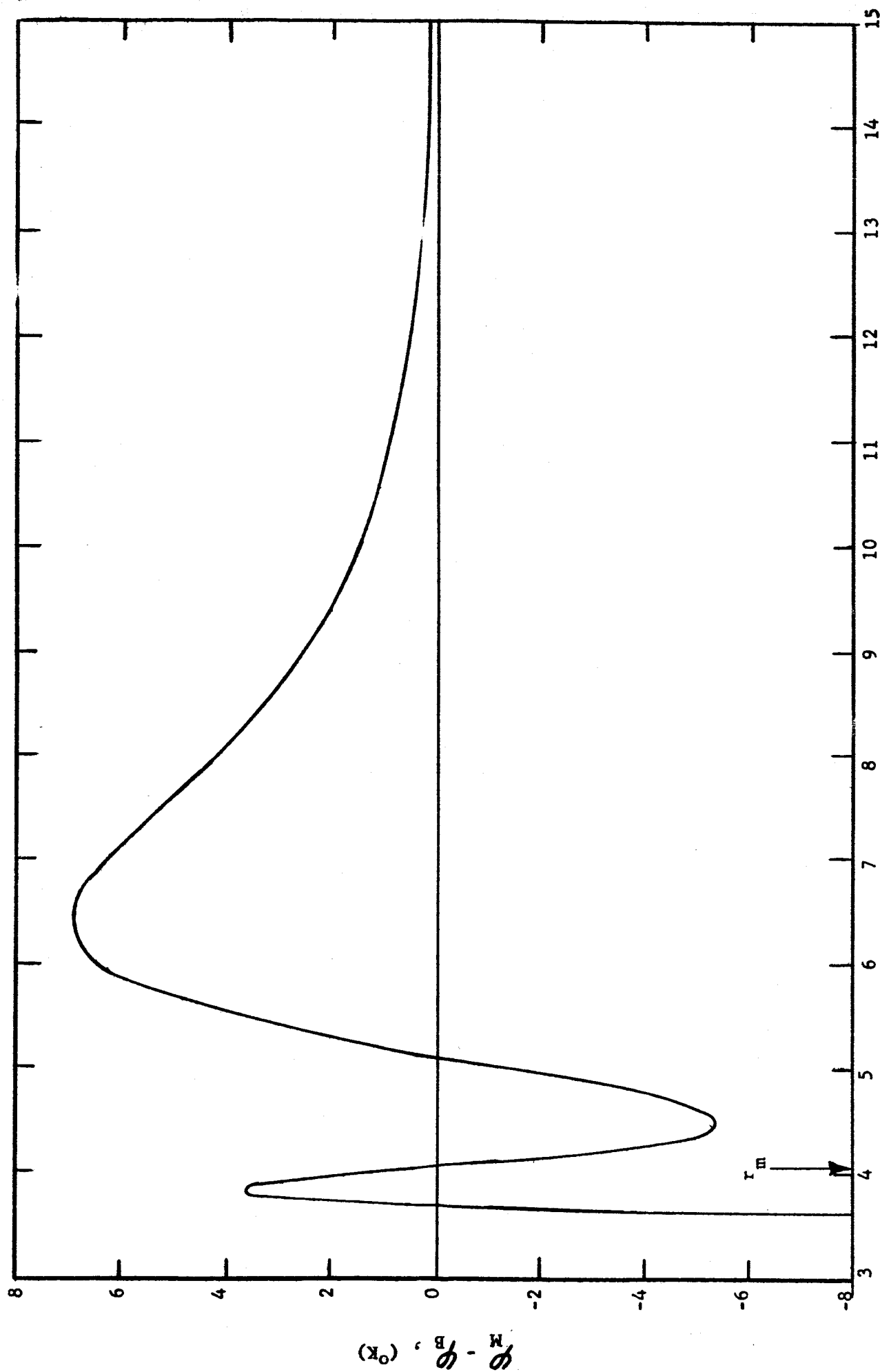


Fig. 24

A Comparison in the Attractive Region of ϕ_B , the Buckingham (exp-6) Potential, with ϕ_M , the "most likely" Morse Potential, for Kr.

Appendix I

Experimental $B(T)$ and $\eta(T)$ Data

The three criteria we use to fix the Morse potential parameters are sensitive in different ways to the data in various temperature ranges. A particularly unsatisfactory situation occurs when data from different laboratories either disagree in their common temperature range or else (in the case of contiguous but non-overlapping temperature ranges) do not join smoothly. In collecting the experimental data used we have drawn heavily on compilations of data in which the raw experimental data has been critically examined and a smoothed set presented. Particularly valuable have been the compilations of $B_x(T)$ by Saville, Byrne and Staveley^a and those of $\eta_x(T)$ by Touloukian and associates^b.

We present in the following tables the $B_x(T)$ and $\eta_x(T)$ used in our calculations, and quote the original sources from which they were drawn.

- - - - -
- a. G. Saville, M. A. Byrne and L.A.K. Staveley, private communication. These compilations were kindly supplied by Dr. L.A.K. Staveley.
 - b. Thermophysical Properties Research Center, Purdue University, Data Book, Volume II. References to this work are abbreviated: TPRC, Table number, date of release of table.

Table A-1 $B_x(T)$ for Ne

T (°K)	$B_x(T)$ (cm ³ /mole)
123.16	1.23
131.94	2.92
170.15	6.30
173.16	6.75
223.16	9.37
273.16	11.12
323.16	12.32
373.16	12.76
473.16	13.43
573.16	13.70
673.16	13.78
773.16	13.74
873.16	13.89
973.16	13.98

Sources of Data: G. A. Nicholson and W. G. Schneider, Can. J. Chem. 33, 589 (1955); L. Holborn and J. Otto, Z. Physik 33, 1 (1925); H. Kamerlingh-Onnes et. al., Commun. Phys. Lab. Univ. Leiden 147d (1915); ibid., 154a (1919).

Table A-2 $\eta_x(T)$ for Ne

T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)	T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)	T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)
33.16	549	210.94	2478	377.60	3702
66.49	1066	222.05	2571	444.27	4110
77.60	1207	233.16	2662	455.38	4175
88.72	1320	244.27	2751	499.83	4425
99.83	1437	255.38	2839	544.27	4663
110.94	1551	266.49	2925	555.38	4722
122.05	1663	277.60	3009	699.83	5444
133.16	1772	288.72	3092	755.38	5714
144.27	1879	299.83	3173	844.27	6150
155.38	1984	310.94	3253	933.16	6601
177.60	2188	333.16	3408	1066.49	7329
188.72	2287	344.27	3483		
199.83	2383	366.49	3630		

Sources of Data: T.P.R.C., Table 2031, December 1962, compiled from: R. S. Edwards, Proc. Roy. Soc. (London) A119, 578 (1928); H. L. Johnston and E. R. Grilly, J. Phys. Chem. 46, 948 (1942); V. D. Majumdar and M. B. Vajifdar, Proc. Indian Acad. Sci. 8A, 171 (1938); A. Nasini and C. Rossi, Gazz. Chim. It. 58, 898 (1928); A. O. Rankine, Proc. Roy. Soc. (London) A84, 181 (1910); M. Trautz and H. M. Binkele, Ann. Physik 5 (5), 561 (1930); M. Trautz and H. Zimmermann, Ann. Physik 22 (5), 189 (1935); M. Trautz and R. Zink, Ann. Physik 7 (5), 427 (1930); A. van Itterbeek and O. van Paemel, Physica 7, 273 (1940); O. van Paemel and Verh Kon Vlaamsche, Acad. Wetensch. Letteren SchooneKunsten Belgic Klasse Wetensch 3 (3), 3 (1941); R. Wobser and F. Muller, Kolloid-Beihfte 52, 165 (1941); H. G. de Carvalho, Anais. Assoc. Quim. Brazil. 4 (2), 79 (1945); J. Kestin and W. Leidenfrost, Physica 25, 1033 (1959); M. Trautz and K. F. Kipphan, Ann. Physik 2 (5), 743 (1929).

Table A-3. $B_x(T)$ for Ar.

T (°K)	$B_x(T)$ (cm ³ /mole)	T (°K)	$B_x(T)$ (cm ³ /mole)	T (°K)	$B_x(T)$ (cm ³ /mole)
84.791	-249.34	138.15	-100.91	323.15	-11.09
88.336	-229.89	143.15	-94.54	348.15	-7.19
92.303	-211.79	148.15	-88.60	373.15	-4.10
95.058	-200.87	153.15	-83.13	398.15	-1.16
101.398	-178.73	163.15	-73.34	423.15	1.28
105.513	-166.06	173.15	-65.18	448.15	3.72
108.146	-160.27	188.15	-54.70	473.15	5.12
113.318	-149.58	203.15	-46.28	573.15	10.74
117.501	-140.58	223.15	-37.24	673.15	15.72
123.99	-127.99	248.15	-28.29	773.15	17.75
128.15	-115.96	273.15	-21.26	873.15	19.47
133.15	-107.99	298.15	-15.63		

Sources of Data: L. A. K. Staveley, private communication, compiled from: A. Michels, J.M.H. Levelt, and W. de Graaff, *Physica* 24, 659 (1958); A. Michels, Hk. Wijker, and Hub. Wijker, *Physica* 15, 627 (1949); E. Whalley, Y. Lupien, and W. G. Schneider, *Can. J. Chem.* 31, 722 (1953); L. Holborn and J. Otto, *Z. Physik* 23, 77 (1924); *ibid.* 30, 320 (1924); L. Holborn and H. Schultze, *Ann. Physik* 47, 1089 (1915); I. P. Ishkin and I. A. Rogavaya, *Zhur. Fiz. Khim.* 31, 410 (1957); B.E.F. Fender and G. D. Halsey, Jr., *J. Chem. Phys.* 36, 1881 (1962).

Table A-4. $\eta_x(T)$ for Ar.

T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)	T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)	T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)
88.72	753	366.49	2635	1055.38	5495
122.05	1009	377.60	2695	1110.94	5663
144.27	1178	422.05	2931	1177.60	5859
166.49	1345	466.49	3160	1277.60	6143
199.83	1594	522.05	3436	1366.49	6392
233.16	1851	566.49	3648	1477.60	6701
255.38	2009	677.60	4142	1577.60	6979
266.49	2081	722.05	4326	1655.38	7195
277.60	2143	766.49	4503	1722.05	7376
288.72	2206	799.83	4631	1777.60	7524
299.83	2268	877.60	4914	1888.60	7800
310.94	2330	910.94	5029	1977.60	7990
322.05	2392	966.49	5214		
344.27	2514	988.72	5286		

Sources of Data: T.P.R.C., Table 2045, December 1961, compiled from:
 A. Michels, A. Botzen and W. Schuurman, *Physica* 20, 1141 (1954);
 F. G. Keyes, Project. Squid. Report 37, 1 (1952) (ATI 167174);
 V. Vasilescu, *Ann. Phys.* 20, 292 (1945); C. F. Bonilla, S. J. Wang,
 and H. Weiner, *Trans. ASME* 78 (6), 1285 (1956); M. Trautz and
 W. Ludewigs, *Ann. Physik.* 3 (5), 409 (1929); J. Kestin and
 H. E. Wang, AFORS TN 56, 23 (1956) (AD 82011); T. Makita, *Rev.*
Phys. Chem. Japan 27, 16 (1957); J. Kestin and W. Leidenfrost
Physica 25, 537 (1959); R. Wobser and F. Muller, *Kolloid-Beihafte*
52, 165 (1941); A. O. Rankine, *Proc. Roy. Soc. (London)* A88, 575
 (1913); M. Trautz and R. Zink, *Ann. Physik* 9, 981 (1931); W. Kopsch,
 Halle Univ. Doctoral Dissertation, 1909; H. Schultze, *Ann. Physik.*
5 (4), 140 (1901); H. L. Johnston and E. R. Grilly, *J. Phys. Chem.*
46, 948 (1942); M. Trautz and H. M. Binkele, *Ann. Physik* 5 (5),
 561 (1930); H. G. de Carvalho, *Anais. Assoc. Quim. Brazil.* 4
 (2), 79 (1945).

Table A-5. $B_x(T)$ for Kr.

T (°K)	$B_x(T)$ (cm ³ /mole)	T (°K)	$B_x(T)$ (cm ³ /mole)
107.547	-386.67	235.1	-88.35
108.894	-374.23	270.3	-66.25
109.938	-365.03	273.15	-62.70
112.279	-349.75	323.15	-42.78
115.351	-330.80	373.15	-29.28
118.498	-314.83	423.15	-18.13
121.467	-301.59	473.15	-10.75
121.641	-297.47	573.15	.42
128.137	-270.49	673.15	7.24
132.126	-255.62	773.15	12.7
138.071	-236.73	873.15	17.19
174.4	-151.5		

Sources of Data: L.A.K. Staveley, private communication, compiled from: E. Whalley and W. G. Schneider, J. Chem. Phys. 23, 1644 (1955); E. Whalley and W. G. Schneider, Trans. Amer. Soc. Mech. Engineers, 76, 1007 (1954); G. Thomaes and R. van Steenwinkel, Nature 193, 160 (1962); B.E.F. Fender and G. D. Halsey, Jr., J. Chem. Phys. 36, 1881 (1962).

Table A-6. $\eta_x(T)$ for Kr.

T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)
144.27	1279
166.49	1470
188.72	1656
210.94	1838
222.05	1928
244.27	2104
266.49	2277
277.60	2362
288.72	2446
333.16	2773
366.49	3010

Sources of Data: T.P.R.C., Table 2020, December 1962, compiled from: I. Amdur, J. Chem. Phys. 16, 190 (1948); A. Nasini and C. Rossi, Gazz. Chim. It. 58, 989 (1928); H. G. de Carvalho, Anais. Assoc. Quim. Brazil. 4 (2), 79 (1945); J. Kestin and W. Leidenfrost, Physica 25, 1033 (1959).

Table A-7. $B_x(T)$ for Xe.

T (°K)	$B_x(T)$ (cm ³ /mole)
273.16	-154.74
323.16	-110.73
373.16	-81.73
423.16	-61.29
473.16	-46.05
523.16	-33.20
573.16	-24.30
673.16	-10.77
773.16	-.13
873.16	7.95
973.16	14.22

Sources of Data: A. Michels, T. Wassenaar, and P. Louwerse, *Physica* 20, 99 (1954); J. A. Beattie, R. J. Barriault, and J. S. Brierley, *J. Chem. Phys.* 19, 1222 (1951); E. Whalley, and W. G. Schneider, *J. Chem. Phys.* 23, 1644 (1955); E. Whalley, Y. Lupien, and W. G. Schneider, *Can. J. Chem.* 33, 633 (1955).

Note: Whenever two or more B values were available at the same, or almost the same temperature, the selected value of B was obtained by a simple interpolation.

Table A-8. $\eta_x(T)$ for Xe.

T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)
277.60	2141
288.72	2224
299.83	2307
310.94	2389
377.60	2862
399.83	3013
455.38	3378
499.83	3655
555.38	3984

Sources of Data: T.P.R.C., Table 2033, December 1961, compiled from: M. Trautz and R. Heberling, Ann. Physik. 20 (5), 118 (1934); A. O. Rankine, Proc. Roy. Soc. (London) A84, 181 (1910); H. G. de Carvalho, Anais Assoc. Quim. Brazil. 4 (2), 79 (1945); J. Kestin and W. Leidenfrost, Physica 25, 1033 (1959); J. Kestin and H. E. Wang, AFORS TN 56, 23 (1956) (AD 82011).

Table A-9. $B_x(T)$ for N_2 .

T (°K)	$B_x(T)$ (cm ³ /mole)	T (°K)	$B_x(T)$ (cm ³ /mole)
90.0	-201.0	248.15	-17.00
111.4	-132.7	273.15	-10.21
123.15	-109.9	293.15	-5.69
126.83	-102.2	298.47	-4.75
128.69	-99.50	303.15	-3.64
133.15	-94.08	323.15	-.47
143.15	-79.46	347.90	3.02
151.96	-69.63	373.15	6.21
163.15	-60.64	398.21	9.19
173.15	-52.73	423.15	11.72
183.15	-45.97	473.15	15.53
192.05	-39.48	573.15	20.44
223.15	-25.90	673.15	23.77

Sources of Data: L.A.K. Staveley, private communication, compiled from: A. Michels, H. Wouters, and J. de Boer, *Physica* 1, 587 (1934); L. Holborn and J. Otto, *Z. Physik* 10, 367 (1922); I. P. Ishkin and M. G. Kaganer, *Soviet Phys. - Tech. Phys.* 1, 2255 (1957); H. Kramerlingh-Ohnes and A. T. van Urk, *Comm. Phys. Lab. Leiden* 169a (1924); R. A.H. Pool, *et. al.* *Trans. Faraday Soc.* 58, 1692 (1962).

Table A-10 $\eta_x(T)$ for N_2

T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)	T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)	T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)
110.94	768	366.49	2068	977.60	3927
144.27	984	377.60	2114	988.72	3954
188.72	1231	399.83	2203	1022.05	4034
199.83	1290	422.05	2289	1077.60	4167
222.05	1406	466.49	2455	1122.05	4271
233.16	1462	522.05	2650	1166.49	4374
255.38	1571	555.38	2761	1222.05	4501
277.60	1677	610.94	2937	1266.49	4601
288.72	1729	677.60	3137	1310.94	4699
299.83	1780	710.94	3232	1333.16	4747
310.94	1830	766.49	3386	1566.49	5212
322.05	1879	810.94	3505	1688.72	5416
333.16	1927	855.38	3621	1710.94	5447
344.27	1975	877.60	3678		
355.38	2022	922.05	3790		

Sources of Data: T.P.R.C., Table 2043, December 1961, compiled from: H. L. Johnston and K. E. McCloskey, J. Phys. Chem. 44, 1038 (1940); H. L. Johnston, R. W. Mattox and R. W. Powers, NACA TN 2546, 1 (1951); J. Kestin and K. Pilarczyk, Trans. ASME 76, 987 (1954); H. Markowsky, Ann. Physik. 14 (4), 742 (1904); P. J. Rigden, Phil. Mag. 25, 961 (1938); C. J. Smith, Proc. Phys. Soc. (London) 34, 155 (1922); M. Trautz and P. B. Baumann, Ann. Physik. 2 (5), 733 (1929); M. Trautz and R. Heberling, Ann. Physik. 10 (5), 155 (1931); M. Trautz and A. Melster, Ann. Physik. 7 (5), 409 (1929); H. Vogel, Ann. Physik. 43 (4), 1235 (1914); K. L. Yen, Phil. Mag. 38, 582 (1913); C. P. Ellis and C. J. G. Raw, J. Chem. Phys. 30, 574 (1959); T. Makita, Rev. Phys. Chem. Japan 27, 16 (1957); F. Lazarre and B. Vodar, Compt. Rend. 243 487 (1956); W. L. Sibbit, G. A. Hawkins and H. L. Solberg, Trans. ASME 65, 401 (1943); V. D. Majumdar and M. B. Vajifdar, Proc. Indian Acad. Sci. 8A, 171 (1938); M. Trautz and R. Zink, Ann. Physik 7 (5), 427 (1930); R. Wobser and F. Muller, Kolloid-Beihafte 52, 165 (1941); M. Trautz and R. Zink, Ann. Physik. 9, 981 (1931).

Table A-11 $B_x(T)$ for CH_4

T (°K)	$B_x(T)$ (cm ³ /mole)	T (°K)	$B_x(T)$ (cm ³ /mole)
108.45	-363.265	373.155	-21.13
125.20	-268.445	398.160	-15.90
149.10	-187.840	423.166	-11.32
186.40	-126.150	448.197	-7.56
223.60	-82.655	473.213	-4.16
249.30	-68.455	498.229	-1.16
273.155	-53.485	523.245	1.49
298.152	-43.04	548.260	3.89
303.152	-40.91	573.274	5.98
323.151	-34.40	598.285	7.88
348.152	-27.25	623.294	9.66

Sources of Data: G. Thomaes and R. van Steenwinkel, *Nature* 187, 229 (1960); H. W. Schamp, *et. al.*, *Phys. Fluids* 1, 329 (1958); D. R. Douslin, *Progress in International Research on Thermodynamic and Transport Properties*. (The American Society of Mechanical Engineers, New York, 1962) p. 135.

Note: In the range 273°K to 423°K where two B_x values were available at the same, or almost the same temperature, the selected value of B_x was obtained by a simple interpolation.

Table A-12. $\eta_x(T)$ for CH_4 .

T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)	T (°K)	$\eta_x(T)$ (10^7 gm/cm sec)
122.05	489	255.38	964
133.16	530	266.49	1002
144.27	571	277.60	1039
155.38	612	288.72	1076
166.49	653	299.83	1112
177.60	693	310.94	1148
188.72	732	322.05	1184
199.83	772	333.16	1219
210.94	811	344.27	1254
222.05	850	355.38	1289
233.16	880	366.49	1323
244.27	926		

Sources of Data: T.P.R.C. Table 2022, September 1960, compiled from: E.W. Comings and R. S. Egly, Ind. Eng. Chem. 33, 1224 (1941); E. W. Comings, B. J. Mayland and R. S. Egly, Univ. of Illinois Eng. Expt. Sta. Bull. 354, 1 (1944); H. Iwasaki and H. Takahashi, J. Chem. Soc. Japan, Ind.Chem. Sec., 62 (7), 918 (1959); F. G. Keyes, Trans. ASME 76, 809 (1954); E. Kuss, Z. angew. Phys. 4, 203 (1953); J. D. Lambert, K. J. Cotton, M. W. Pailthorpe, A. M. Robinson, J. Scrivins, W. R. F. Vale, and R. M. Young, Proc. Roy. Soc. (London) A231, 280 (1955); H. L. Johnston and E. R. Grilly, J. Phys. Chem. 46, 948 (1942); M. Trautz and A. Melster, Ann. Physik 7, (5), 409 (1929).